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Supercritical Fluid (SCF) Technologies: Assessment of Applicability to Installation Restoration Processes

Report No. SFIM-AEC-TS-CR-93127

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USAEC has conducted an evaluation of Supercritical Fluid (SCF) technologies for their applicability to treatment of explosives, chlorinated hydrocarbons, and metals in soils, water, and/or waste sludge media. Off-specification explosives and propellants that have traditionally been open burned or open detonated were also examined.

Supercritical fluids are substances which have been heated and compressed to above their critical temperatures and pressures and possessing unique transport and mass transfer properties. Supercritical fluid extraction (SFE) used the solvating properties of supercritical fluids to extract one or more organic components from a mixture into a supercritical solvent (commonly CO_2). The concentrated extract stream may then be recycled, reclaimed, or destroyed by other methods. Supercritical water oxidation destroys the organics compounds in a mixture, leaving innocuous end products.

A literature search was conducted to determine the current status of SCF technology development. Removal or destruction of the contaminants present in the selected waste scenarios was evaluated, although only limited treatability and economic information was available for these compounds. OB/OD treated waste, explosives-contaminated lagoon sediment, and soil contaminated with solvents and petroleum products were determined to be technically feasible. Additional process development may be required to address current operational limitations and optimize process economics.

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SUPERCRITICAL FLUID (SCF) TECHNOLOGIES: ASSESSMENT OF APPLICABILITY TO INSTALLATION RESTORATION PROCESSES

FINAL REPORT

Contract Number DACA 31-91-D-0079

Prepared for:

U.S. Army Environmental Center (USAEC)
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EXECUTIVE SUMMARY

As part of its mission to evaluate and develop cost-effective treatment programs to meet the goals of the Army's environmental program, the U.S. Army Environmental Center (USAEC) has conducted an evaluation of Supercritical Fluid (SCF) technologies for their applicability to treatment of hazardous wastes generated at Army production, maintenance, and training facilities. Waste scenarios selected for SCF evaluation include explosives, chlorinated hydrocarbons, and metals in soils, water, and/or waste sludge media. Additionally, off-specification explosives and propellants that have traditionally been open burned or open detonated were examined.

Supercritical fluids are substances that are heated and compressed to above their critical temperatures and pressures. Under such conditions, these fluids exhibit unique properties with respect to their transport and mass transfer properties which render them potentially useful for destruction or extraction of contaminants from wastes or environmental media. Supercritical fluid extraction (SFE) uses the solvating properties of supercritical fluids to extract one or more organic components from a mixture into a supercritical solvent (commonly CO_2). The concentrated extract stream may then be recycled, reclaimed, or destroyed by other methods. Supercritical water oxidation (SCWO) destroys the organic compounds in a mixture, leaving innocuous end products.

A literature search has been conducted to determine the current status of SCF technology development. As appropriate, SCF experts have been contacted for additional information. The potential applicability of SCF technologies to the specified waste scenarios has been evaluated based on a set of technical and economic criteria.

Both SFE and SCWO units are available at the pilot-scale. Removal or destruction of the contaminants present in the selected waste scenarios has not been widely investigated.

Because of the limited treatability and economic information, testing and additional economic evaluation should be conducted prior to initiating a potential demonstration project. The waste scenarios showing technical potential for further study were determined to be:

- OB/OD treated waste.
- Explosives-contaminated lagoon sediment.
- Soils contaminated with solvents and petroleum products.

Although, based on preliminary information, these scenarios will result in relatively high treatment costs, additional development and/or treatment scenario optimization may result in a cost reduction, potentially making SCWO a cost-effective alternative for specific applications. Under conditions where regulatory constraints restrict the use of conventional technologies, SCF treatment may become an attractive alternative.

SECTION 1

INTRODUCTION

The U.S. Army Environmental Center (USAEC) is responsible for the evaluation and development of cost-effective treatment technologies to meet the goals of the Army's environmental program. In support of this mission, USAEC has conducted an evaluation of supercritical fluid (SCF) technologies for their applicability to treatment of hazardous wastes generated at Army production, maintenance, and training facilities. These facilities may generate a variety of hazardous wastes as part of routine operations. Historically, disposal practices for such materials included disposal in lagoons and landfills, as well as incineration. Current regulatory programs under the Resource Conservation and Recovery Act (RCRA) require more definitive management of hazardous wastes being generated. As a result, such wastes are currently managed in accordance with RCRA standards. The Army evaluates technologies to provide improved waste management under these standards. Furthermore, remediation of areas contaminated by past waste disposal practices will be necessary under either RCRA Corrective Action or the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA).

This report contains the findings of this evaluation of the current status of SCF technologies for these environmental protection applications. Such technologies were evaluated in 1982 by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA, now USAEC) and were considered to be not yet cost-competitive with other waste management technologies[1]. USAEC has determined that further evaluation of SCF technologies is appropriate in light of technical advances made since the previous evaluation as well as changing regulatory conditions.

Supercritical fluids are substances that are heated and compressed to above their critical temperatures and pressures[2]. The critical temperature and pressure is the highest point at which a substance can exhibit liquid-vapor equilibrium. Above this point, liquid cannot be condensed from the vapor. Under such conditions, these fluids exhibit unique properties with respect to their transport and mass transfer properties which render them potentially

useful for extraction and recovery (or destruction) of contaminants from wastes or other environmental media. Three general areas of potential application include[2]:

- <u>One step separation</u>, for the direct extraction of (generally) high concentration contaminants from wastes.

- <u>Two step separation</u>, where SCFs are used to extract contaminants from other media such as granular activated carbon (GAC) that were used to concentrate the contaminants from dilute wastestreams, such as water. Under such conditions the sorption capacity of the GAC is regenerated by the SCF.

- <u>Reactive separation</u>, where the SCF both extracts the contaminant and serves as a medium for its chemical transformation or destruction. The most common such use of these technologies is supercritical water oxidation (SCWO).

While not truly a supercritical fluid application, wet-air oxidation (WAO) is a related technology that has been available for a number of years. This will not be evaluated as part of this report.

The wastestream treatment applications for which the Army wishes to consider using SCF technologies include, among others, the following:

- Removal of explosives, chlorinated hydrocarbons, and metals from contaminated soils and water.

- The management and treatment of hazardous wastes from current industrial operations at Army Ammunition Plants (AAPs) and Army Depot Activities (ADAs).

- As an alternative to open burning/open detonation (OB/OD) currently practiced as a disposal method for waste explosives.

Typical AAP industrial operations that may generate such wastes include explosive and propellant production, loading, and packing procedures. Army Depot maintenance activities include electroplating, degreasing and cleaning operations, as well as stripping and painting operations.

In this study, the potential applicability of SCF technologies was evaluated for the waste management scenarios described above. The following major tasks were conducted in performing this evaluation:

- Development of representative AAP/ADA waste management scenarios to serve as a basis for technical and economic evaluation.

- Review of technical literature on SCF technologies, focusing upon, but not limited to, the waste types/scenarios described above and the technical developments for SCFs since the previous evaluation[1].

- Site visits and telephone interviews with selected vendors and technical experts in the application of SCF technologies.

- Technical evaluation of SCF technologies for these waste management scenarios, guided by specific evaluation criteria.

- Economic evaluation of SCFs, using the available cost information and the representative waste scenarios defined above.

The results of this evaluation are summarized in this report.

SECTION 2
WASTE SCENARIO DEVELOPMENT

2.1 METHODOLOGY

In order to evaluate the potential technical and economic applicability of supercritical fluid technologies, waste scenarios were developed that represent potential situations at Army installations. The waste scenarios selected include explosives, chlorinated hydrocarbons, and metals contaminated wastes in soils and water. Additionally, off-specification explosives and propellants that have traditionally been open burned or open detonated were examined.

During the waste scenario development, several information sources were consulted[3,4,5,6,7]. The waste scenarios developed were based on the waste types which, under the Reliance Program, are within the Army Research and Development Program's realm of responsibility. Waste quantities, compositions, media, and current disposal practices were determined from USAEC documentation. The scenarios developed represent the best available data and will be considered to be typical wastes for the purposes of this report.

These scenarios were developed based on potential needs for Army installations. The potential applicability of supercritical fluid technologies to these waste streams will be evaluated in Section 4.

2.2 TYPICAL WASTE SCENARIOS

Using the methodology described in Subsection 2.1, representative waste scenarios were developed for paint sludges and solvents, OB/OD operations, electroplating waste, explosives-contaminated soils and sediments, and explosives repacking plant wastewaters. These representative waste scenarios are presented in Table 2-1.

Table 2-1

Representative U.S. Army Waste Scenarios for SCF Applications

Waste(Form)	Quantity/Flow	Composition	Reference
Waste Paint/Solvent (Liquid)	33,000 gallons/year	Solvent: chlorinated hydrocarbons or MEK Paint: 50% by weight organic (epoxy or polyurethane) 50% inorganic 10% Iron Oxide 10% Titanium Dioxide 10% Chromium Oxide 20% Magnesium Silicate (based on combination of colors)	"Development of a New Process for Treatment of Paint Sludge Wastes," Final Report. Ref. No. AMXTH-TE-CR-87141, December 1987.
Spent Chemical Strippers/Paint Sludge (Liquid and sludge)	5,500 gallons/year		
OB/OD[f] (Solid)	456 tons per year[a]	90% RDX[e] 10% HMX	Dr. Roger Schneider (personal communication) Rho-Sigma Associates (re: Holston AAP)
OB/OD Demobilization (Solid)	15,000 tons[g]	Various explosive materials	Crane Robinson (personal communication) U.S. Army - Armament Research, Development and Engineering Center
Electroplating Waste (Liquid)	Total of 27 million gallons/year of sludge in 23 facilities (average 1.2 million gallons/year per facility)	Metal Concentration (mg/L) Cadmium 12 Chromium 18 Copper 12 Nickel 6 Lead 3 Silver N/A Zinc 3 Cyanide 15	Hazardous Waste Minimization Program - Progress Report 1991. Army Materiel Command, November 1992.

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Table 2-1

Representative U.S. Army Waste Scenarios for SCF Applications
(Continued)

Waste(Form)	Quantity/Flow	Composition		Reference
Lagoon Sediment (Solid)	3,900 yd^3	7,000 ppm TNT 200 ppm HMX 30 ppm RDX 5 ppm DNT[b] <10 ppm TNB[c]		WESTON, "Windrow Composting Demonstration for Explosives-Contaminated Soils at the Umatilla Depot Activity, Hermiston, Oregon." Prepared for USAEC, Report No. CETHA-TS-CR-93043, August 1993.
Repacking Plant Wastewater (Liquid)	1,040,000 gallons/year	Parameter COD Lead NO$_3$-N pH	Concentration (mg/L) 10,500[d] 160 1,200 12.5 (pH units)	"A Case Study for the Treatment of an Explosives Wastewater from an Army Ammunitions Plant," Shelby, Lankford, and McCollum. Proceedings of the 39th Industrial Waste Conference, Purdue University.
Contaminated Soil (Solid)	Site Specific	Contains: chlorinated hydrocarbons *metals* explosives Concentrations are site specific		Personal Communication, USAEC.

[a]Although more waste is generated, this is the quantity in a form that would be applicable to treatment by SCF technology.
[b]Sum of 2,4-DNT and 2,6-DNT concentrations.
[c]Value was below detection limit.
[d]Contains RDX, but the entire chemical oxygen demand (COD) may not be attributable to RDX.
[e]Although RDX and HMX are the only constituents of this particular waste, other explosives, such as TNT, may also be present in other potential OB/OD wastes.
[f]This waste is assumed to be generated at 4 facilities and treated in a centralized RCRA Treatment Storage and Disposal (TSD) facility.
[g]Centralized facility to treat existing stockpile in a 3-year time frame.

2.2.1 Waste Paint/Solvent/Paint and Stripper Sludge Scenarios

In the area of paint wastes and solvents, based on data from Letterkenny Army Depot (LEAD)[3], it was determined that several classes of paint wastes potentially exist. These wastes include[1]:

- Spent blast media waste.
- Excess paint and solvent residues.
- Spent spray booth filters.
- Spent solvent strippers/paint sludges.

The spent blast media wastes are generated as a result of paint stripping methods employing sand, walnut shells, steel shot, and potentially plastic blast media. The spent spray booth filters are generated during periodic filter replacement. Excess paint and solvent residues result from painting operations and cleaning of painting equipment. The spent solvent strippers and paint sludge wastes are generated as a result of chemical stripping techniques.

Paints and solvents used at LEAD may be categorized as[3]:

- Primers (generally epoxies).
- Chemical Agent Resistant Coatings (CARC) (polyurethane paints).
- Other paints (epoxies/polyamides).
- Solvents (methyl ethyl ketone and other thinners).

Approximately 33,000 gallons per year of RCRA-regulated waste paint and solvent are currently disposed of by LEAD. An additional 5,500 gallons per year of paint sludge and spent chemical strippers are generated. The solvents and thinners are considered to be chlorinated hydrocarbons (potentially methylene chloride) and methyl ethyl ketone (MEK). The paint consists of approximately 50% organics (epoxy or polyurethane) and 50% inorganic constituents (iron oxide, titanium dioxide, chromium oxide, magnesium silicate). The inorganic content of the paint waste was based on a combination of colors used at LEAD and is assumed to contain iron oxide, titanium dioxide, chromium oxide, and magnesium silicate. Inorganic content varies with paint color[3].

Because of the high temperatures and pressures necessary for supercritical fluid processing, it is unlikely that the spent spray booth filters could be processed under supercritical conditions and, therefore, they were not considered as part of the typical waste stream. Processing restrictions for supercritical fluid extraction and supercritical water oxidation are discussed in greater detail in Sections 3 and 4.

2.2.2 OB/OD Treated Waste Scenario

OB/OD treated waste information was varied. Common practices have allowed for OB/OD of many material types including off-specification explosives and propellants, materials contaminated during explosive and propellant processing (including wood, personal protective equipment, machinery, and spilled manufacturing materials), and off-specification munitions[4]. Although approximate quantities of materials are available for these varied wastes, the economic impact of using existing washout facilities as a pretreatment step to SCF processing was not quantified, so off-specification materials were not considered for economic evaluation within the scope of this project. However, the potential does exist for treatment of those materials by SCF processing. As will be discussed more fully in Sections 3 and 4, safety concerns may make supercritical fluid extraction of explosives impractical. Supercritical water oxidation processes are usually conducted under continuous flow conditions[8]. Only materials that can be suspended, dissolved, or slurried in water can be treated continuously by Supercritical Water Oxidation (SCWO). Contaminated solid materials from manufacturing and processing operations, as well as items such as used shell casings, would not be readily treatable by continuous SCWO technologies. Although it may be possible to render these materials into fine enough particles to allow them to be slurried and pumped, the materials preparation steps required could make the process cost prohibitive. Additionally, clogging problems in the system valves are likely to occur. Although batch SCWO processing has not been widely reported, except at the bench-scale, batch SCWO processing would theoretically be possible and may be economically advantageous in certain circumstances, such as when costly pretreatment steps are required prior to continuous processing.

With these potential constraints in mind, two potential OB/OD treated wastes were chosen as potential candidates for supercritical fluid technology treatment. The first waste selected was a combination of hexahydro-1,3,5-trintro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) as produced at Holston AAP[4]. The material involved has been classified as off-specification because ferrous metal debris was detected. This material is currently disposed of by OB/OD[4].

Approximately 114 tons of off-specification explosive material is destroyed by OB/OD each year at Holston AAP. This material contains 90% RDX and 10% HMX by weight[4]. This material is in a form potentially amenable to supercritical fluid processing as it could safely be size-reduced and slurried in water or hydrolyzed and solubilized in water for treatment[4]. Because of the small quantity of material to be processed from a single Army Installation, a centralized facility processing OB/OD waste from 4 sites will be considered for economic evaluation. The 4 sites are all considered to have the same quantity and type of waste amenable to SCF treatment yielding a total quantity of 456 tons/year of OB/OD waste to be processed. Safety issues associated with the pretreatment would need to be addressed prior to implementation.

The second waste selected for evaluation was a portion of waste currently stockpiled by the Army to be treated by OB/OD [4a]. This material contains various explosives and under the assumed scenario would be processed in a centralized facility. It was assumed that approximately 15,000 tons of stockpiled material would be treated in a 3-year period.

2.2.3 Electroplating Waste Scenario

A total quantity and average composition of electroplating wastes were available for 23 facilities[5]. The average flow per facility and average composition were taken as a typical waste stream. The total quantity for all 23 facilities was 27 million gallons per year of electroplating waste sludge [5]. Based on this information, each facility produces an average of 1.2 million gallons per year of electroplating waste sludge. The average stream is largely inorganic and contains cadmium, chromium, copper, nickel, lead, zinc, and cyanide[5].

2.2.4 Lagoon Sediment Scenario

As a result of standard explosives manufacturing or washout procedures, many installations have lagoons containing explosives-contaminated sediments. Umatilla Depot Activity (UMDA) was selected to be the typical waste scenario for this application because the quantity and concentration of contaminated sediment is well characterized[6].

The waste scenario chosen to represent the contaminated soil case consists of 3,900 yd^3 of sediment containing 7,000 ppm 2,4,6-trinitrotoluene (TNT), 2,000 ppm RDX, 300 ppm HMX, 5 ppm dinitrotoluene (DNT), and <10 ppm 1,3,5-trinitrobenzene (TNB)[6].

2.2.5 Repacking Plant Wastewater Scenario

Wastewater from explosives repacking operations was considered. Information regarding waste stream quantity and composition in a midwestern AAP was available through open literature[7]. The waste stream has been characterized based on Chemical Oxygen Demand (COD), and is known to contain RDX. The typical repacking plant wastewater was selected at an average flow of 4,000 gallons per day[7]. The stream has a COD of 10,500 mg/L. A portion, but not necessarily all, of this COD is attributable to RDX. The stream also contains lead and nitrate[7].

2.2.6 Contaminated Soil Scenario

Finally, contaminated soils from various past manufacturing or operating practices exist at many Army installations. The quantities and contaminant concentrations of these soils are highly site-specific. For purposes of discussion, the contaminants that were considered to be present in these soils were explosives, chlorinated hydrocarbons [including polychlorinated biphenyls (PCBs)] and metals (including lead and chromium). These contaminated soils have traditionally been treated by soil washing, landfilling or incineration. Soil quantities and contaminant concentrations must be determined on a site-by-site basis.

SECTION 3

LITERATURE REVIEW AND TECHNOLOGY DISCUSSION

3.1 METHODOLOGY

In order to evaluate the current status of supercritical fluid technologies, a search of the available research and technical literature was conducted. To ensure a thorough, complete search, the following computerized databases were searched:

- Energy, Science, and Technology (U.S. Department of Energy).
- Scisearch (Institute for Scientific Information).
- Engineered Materials Abstract (ASM International).
- PASCAL (CNRS/INIST, Institute of Information, France).
- CA Search (Chemical Abstracts Service).
- EI Compendex Plus (EI Engineering Information, Inc.).

In order to optimize the search and focus upon recent developments pertinent to the Army's potential needs, the literature search was conducted in stepwise fashion. The initial search focused upon literature from the past 10 years. As a first screening, the following key words and phrases were searched:

- Supercritical fluids, or
- Supercritical extraction, or
- Supercritical water oxidation, or
- Supercritical water destruction.

This search resulted in more than 12,000 abstracts related to supercritical fluid technologies for various applications. From this extremely large information base, the search was focused on the Army's needs by the addition of the following key words:

- Explosives, or
- Hydrocarbon, or
- Metal.

This search resulted in 2,500 potentially pertinent abstracts. These additional key words were added to further focus attention in the potential Army applications:

- Remediation, or
- Treatment, or
- Disposal.

This search resulted in 481 abstracts which were reviewed. Each abstract contained information about the author and bibliographic sources, and language of publication as well as a synopsis of the article. Sources listed included technical journals, conference proceedings, and books. Using the information gathered from the abstracts, 125 articles were selected and obtained. The results of the review of these articles and other literature are described in Subsections 3.2 and 3.3.

Concurrently with the literature review process, a search was made for contacts in industry and academia that could provide additional information in the area of supercritical fluid technologies. Since publication cycles may be lengthy and economic information tends to remain unpublished, personal communication was considered to be an important tool for obtaining much of the current information needed for this analysis.

To assist in locating vendors in the areas of Supercritical Fluid Extraction (SFE) and SCWO, the United States Environmental Protection Agency's (EPA) Vendor Information System for Innovative Treatment Technologies (VISITT) database was used. This database supplied information on vendor experience and contacts for each technology.

University experts were obtained by contacting academic authors cited in the computerized literature search. Each individual that was contacted was asked to supply additional contacts in their field of expertise, both in the academic and industrial sectors. Telephone interviews were conducted with various contacts. As a result of the telephone interviews, site visits to selected universities and technology firms were conducted. The results of visits are presented in Subsection 3.4.

3.2 SUPERCRITICAL WATER OXIDATION

Supercritical water oxidation (SCWO) is a destruction process that utilizes water above its vapor-liquid critical point of 374 °C and 22.1 MegaPascals (MPa) (705 °F and 3,205 pounds per square inch absolute (psia)) to essentially completely oxidize organic materials to carbon dioxide (CO_2), water and other environmentally innocuous reaction products [11, 12]. In contrast to WAO, which is conducted at subcritical temperatures and pressures, SCWO is capable of complete destruction of contaminants in an aqueous stream.

SCWO processes can be applied to water containing 25% or less organic waste by weight. In the concentration range of 2 to 25% organics, the SCWO process is autogenous, that is, it is a self-sustaining reaction. Above 25% organic content, the oxidation process produces excess heat that must be removed to maintain the targeted operating parameters. Within the autogenous range, SCWO has been reported to be more cost effective than incineration [13]. Additionally, because SCWO processing occurs at a lower temperature, and often without the presence of excess nitrogen, than the processing conditions required for incineration, hazardous emissions of substances such as nitrogen oxides (NO_x), and acid gases associated with incinerator operation are avoided. Reduced air emissions and lower operating temperatures may result in lower costs for SCWO processing compared to incineration.

3.2.1 Background

Water is present under normal conditions as liquid water, ice or steam. Upon heating water to temperatures and pressures above the critical point, 374 °C (705 °F) and 22.1 MPa (3,205 psia), a new fluid state of water emerges [11]. Under these conditions, water is a fluid that is neither a liquid nor a gas but a homogeneous mixture having characteristics of the two. Figure 3-1 is the Temperature-Pressure diagram for water, showing the location of the liquid, gas, solid, and supercritical phases for water. At supercritical conditions, the properties of water are substantially different than they are under normal conditions. The density, dielectric constant, hydrogen bonding, and other physical properties change

PRESSURE (psia)

Supercritical Fluid

Liquid

Solid

0.09 psia

Triple Point of Water

Critical Point (T_cP_c)

Gas

Gas

TEMPERATURE (°F)
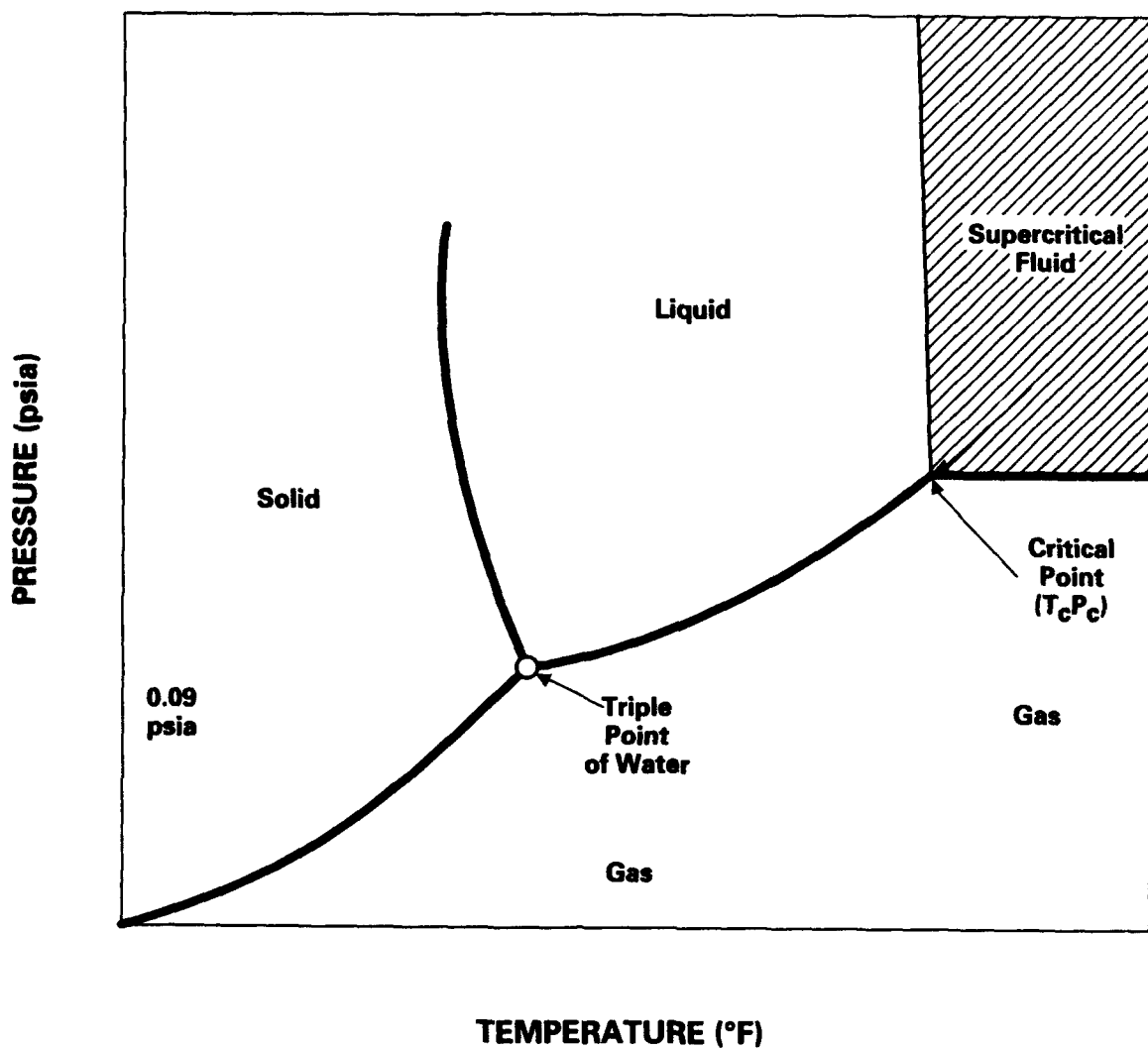
Not To Scale

FIGURE 3-1   PHASES OF WATER AT MODERATE PRESSURES

significantly with the result that the Supercritical Water (SCW) behaves very much like a moderately polar solvent [15]. The change in these properties with temperature from the subcritical to supercritical region is depicted in Figure 3-2. As the water temperature increases from ambient to near the critical point, hydrocarbon solubility increases dramatically while inorganic solubility substantially decreases. The fluid density decreases and continues to decrease within the supercritical region.

Under these conditions, water is an excellent solvent for organic substances and becomes highly miscible with gases, such as oxygen, creating a single, homogenous reaction mixture [16]. The advantage of this homogeneous mixture is that mass transfer is not a limit to reaction. Also, inorganic salts are only slightly soluble in SCW under these conditions and precipitate as solids [17]. If these salts are not separated under supercritical conditions, they will redissolve to their saturation limit when the fluid returns to subcritical conditions. Once in solution, the viscosity of SCW is almost gas-like (more than 20 times below room-temperature viscosity), which creates an increase in the diffusion coefficients such that the SCWO reaction rates are controlled by reaction kinetics and not mass transfer [18, 17]. This unusual combination of thermodynamic and mass transport properties provides for excellent single-phase contact between the organic material and the oxidant source that facilitates rapid and complete oxidation reactions, resulting in the formation of water, CO_2, and inorganic salts [19, 20]. Reaction rates have been reported to be at least one and possibly two orders of magnitude higher than at subcritical temperatures [21]. Predictive modeling of the behavior of water in supercritical conditions has been well summarized [1].

3.2.2 Process Description

The basic steps of the SCWO process as shown in Figure 3-3 involve the mixing and blending of the feed material to form an aqueous solution or slurry of waste with water, supplemental fuel (e.g., methanol) if necessary, and any chemical additives such as pH neutralizing agents. The feed is then mixed with the oxidant source such as oxygen, air, or hydrogen peroxide, and fed to the reactor via a high-pressure feed pump. A specialized pump is required if slurried solid waste (such as soil) is to be treated. The mixture is often
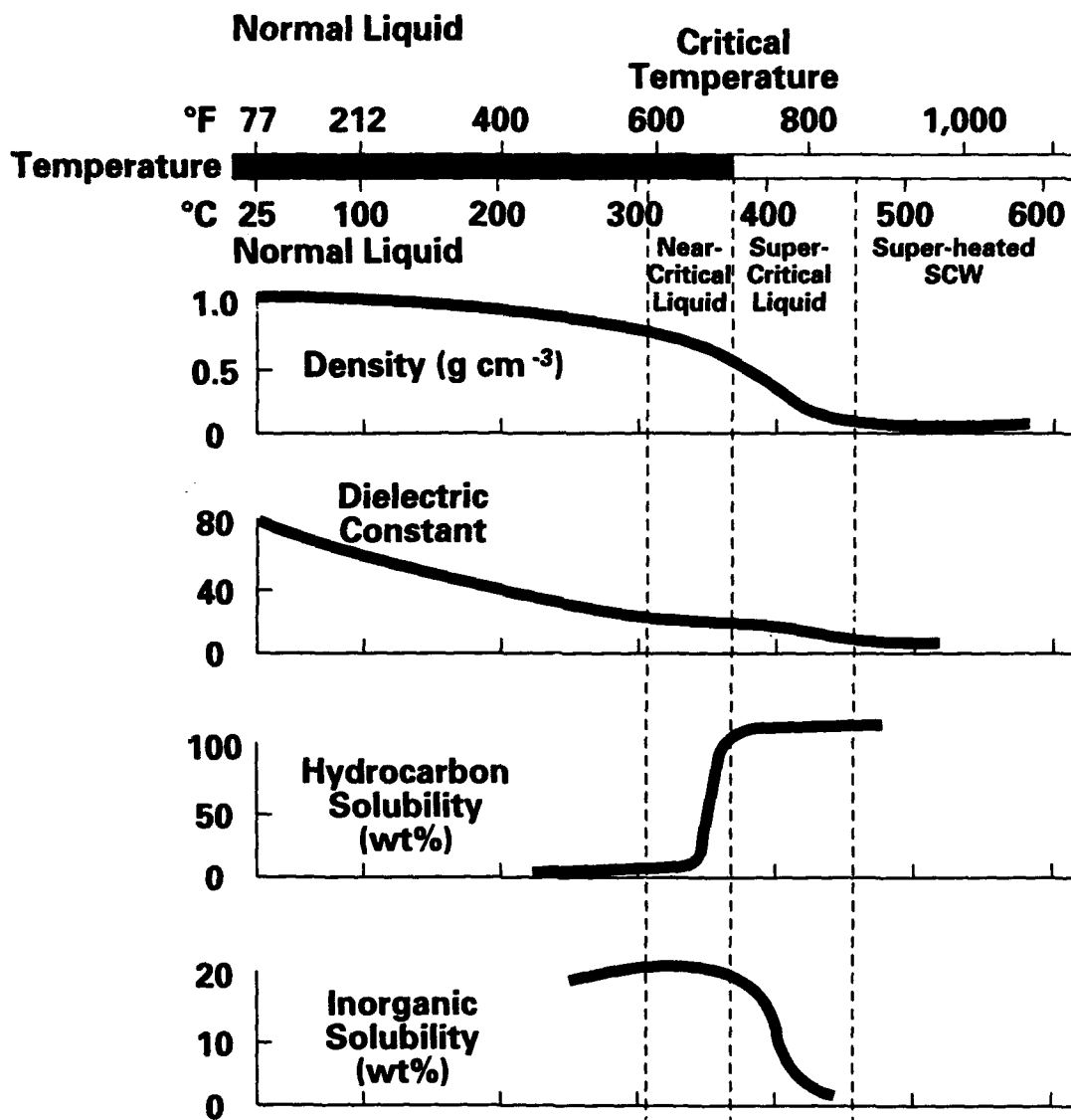
FIGURE 3-2   PROPERTIES OF WATER AT VARYING TEMPERATURES (PRESSURE RANGE 218.3 300 ATM)
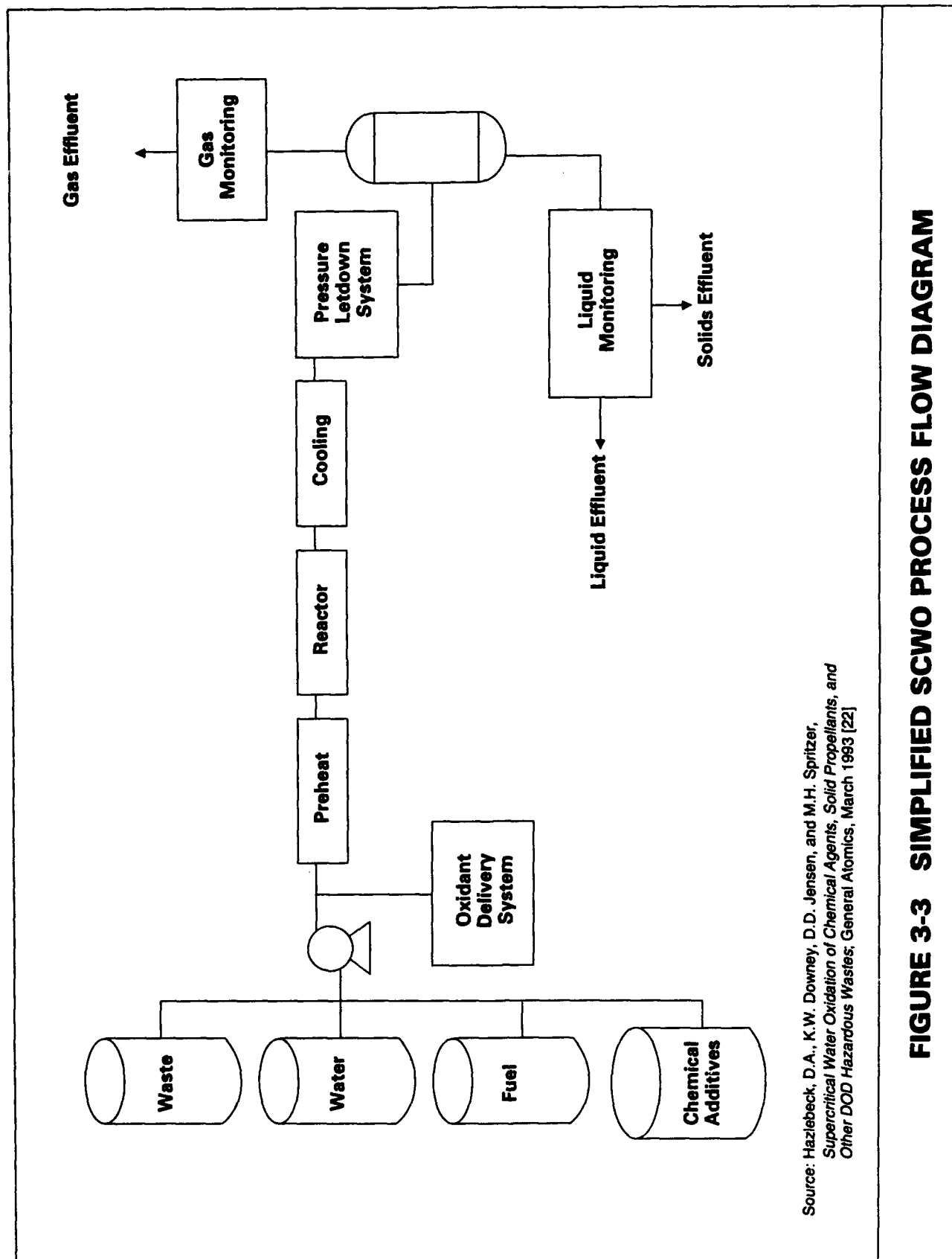
Source: Hazlebeck, D.A., K.W. Downey, D.D. Jensen, and M.H. Spritzer, *Supercritical Water Oxidation of Chemical Agents, Solid Propellants, and Other DOD Hazardous Wastes*, General Atomics, March 1993 [22]

FIGURE 3-3 SIMPLIFIED SCWO PROCESS FLOW DIAGRAM

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preheated prior to introduction into the reactor to ensure that supercritical temperatures and pressures are maintained. This preheating is often accomplished by passing the feed through a heat exchanger, allowing the hot effluent to transfer heat to the cold influent after the initial startup period. The reactors generally consist of long cylindrical, continuous flow reactors. The reactor diameter is limited by heat transfer constraints as well as fluid flow considerations. In the case of wastes that contain solids (such as a soil slurry) or wastes that will generate solids during oxidation (such as waste with inorganic constituents which will form insoluble salts under supercritical conditions), a sufficient fluid velocity must be maintained such that particle settling does not occur within the pipe. A new, down-flow reactor as shown in Figure 3-4 has been developed by Modar [23]. In this patented process, the waste is fed down into the reactor and the effluent is discharged from the top of the reactor with solids settling out in the bottom of the reactor. Additionally, physical separation techniques to remove solids while the solution is in the supercritical state are currently being developed [4].

As the supercritical mixture exits the reactor, the effluent is cooled by passing it through a heat exchanger which preheats the feed and then the pressure is lowered to ambient conditions. This pressure release is performed rapidly in a flash separator, which results in the vaporization of the dissolved gases. The vaporized gases exit from the top of the separator, while the residual liquid drops to the bottom of the separator from where it is transferred for testing, storage, and subsequent discharge. The use of the temperature and pressure of the effluent mixture from the reactor to generate electricity by passing it through a turbine has been investigated, but has not yet been used economically.

3.2.3 Applicability of SCWO

SCWO is applicable to all oxidizable organic materials and cyanides. Inorganic materials are not destroyed by SCWO, but often form salts that are insoluble in supercritical conditions and thus could be separated from solution. The forms of waste that can be treated by this process include slurries, soils, and solids which can be slurried, sludge wastes which can be solubilized in water, and aqueous streams. Research has also been
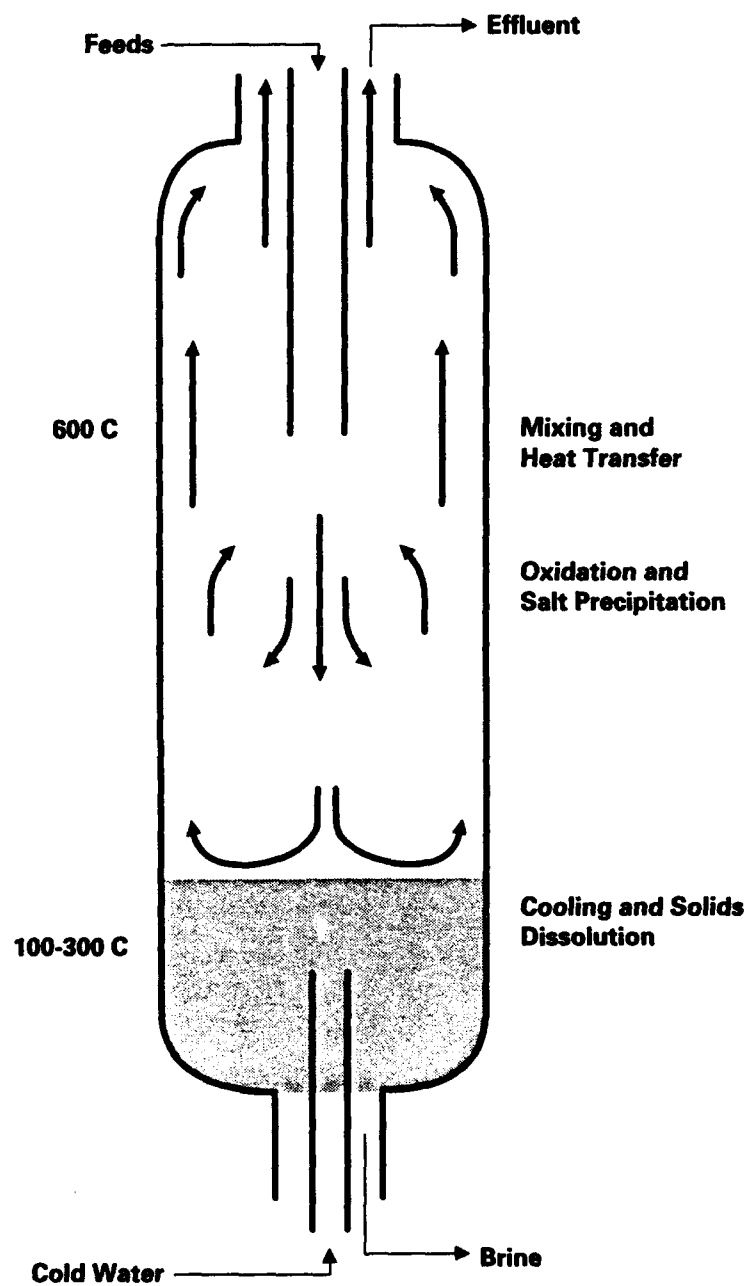
Feeds → Effluent

600 C — Mixing and Heat Transfer

Oxidation and Salt Precipitation

100-300 C — Cooling and Solids Dissolution

Cold Water → Brine

FIGURE 3-4   MODAR VESSEL REACTOR CONCEPT

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conducted for NASA on SCWO of wastes consisting of human urine, feces, and wipes for potential use in space applications [24].

It is usually preferable that the waste feed material be pumpable because of the economic advantage of having a continuous process [8]. The use of batch reactors to treat the materials may not be cost effective in some circumstances as a result of the energy costs associated with repeatedly bringing the reactor to the high temperature and pressure required for the reactions and the increased labor required for batch processing [8]. Batch processing of materials not amenable to continuous flow reactors may be possible. Then potential economic benefits of batch processing must be evaluated on an individual basis. Organic solids, including some types of wood [11], can often be dissolved in the supercritical water, but the time required for them to solubilize in the SCW becomes a limiting factor when considering residence time and reactor size [25]. Therefore, material feed size will have an effect on the types of wastes that can be treated continuously by SCWO and some materials may require size reduction to allow for dissolution and oxidation in the reactor within the minimum residence time for the reactor. Therefore, when a solid material is continuously fed to the reactor, it usually undergoes a size reduction step for convenience of incorporation into the feed as a pumpable slurry [26]. Research conducted at Los Alamos National Laboratory investigated the feasibility of slurrying explosive waste prior to feeding it to the SCWO reactor [27]. The research indicated problems with using a slurry because the slurried particles can react rapidly during the pumping process [27]. The use of a low temperature alkaline hydrolysis pretreatment step was recommended for explosives prior to treatment by SCWO. The hydrolysis step decomposes the explosive material into water-soluble non-explosive products. This hydrolysis step is advantageous because it eliminates the reactivity risk associated with pumping slurried explosives particles, solubilizes the solid material, and eliminates the potential for plugging the reactor with the slurried particles.

The concentration of the oxidizable organic material in the feed stream is important because the heat of oxidation is released within the fluid and results in a temperature rise of the fluid within the reactor which helps to sustain the reaction. While the preferable

concentration of organic material present in the feed ranges from 2 to 25% by weight of the water [26], optimization of the process indicates that feed heating value of 1,900 Btu/lb is required for the reactions to continue on a self-sustaining basis [28, 23]. The Btu content may be supplied by the waste alone or a supplemental fuel source may be added to the waste feed. For low levels of organics (less than 1%), the cost of supplying the heat required to oxidize the small amounts of organics may become uneconomical and biological or activated carbon treatment may be more appropriate [28, 25]. In cases where the fuel value of the waste feed to the reactor does not meet heat content specifications, blending of higher fuel value wastes, adding alternative fuel sources such as methanol, MEK, isopropyl alcohol, or other hydrocarbons, or preheating the feed stream may be necessary to sustain sufficient temperatures within the reactor. Calculations for bulk propellants, explosives and pyrotechnics (PEPs) indicate that, based upon heats of combustion, the aqueous feed to the SCWO reactor should contain 5 to 10% by weight explosives to provide self-sustaining conditions [27]. This concentration is within the range generally considered by USAEC to be safely handled without threat of propagation should an explosion occur. However,the upper end of this range approaches the boundary of safe handling, so caution would be needed to minimize concentration fluctuations [28a].

Supplemental oxidant sources, such as oxygen, hydrogen peroxide, or air, are used to promote the oxidation reactions. The oxidant can be fed directly into the reactor or mixed with the feed prior to introduction into the reactor [17]. It is reported that essentially complete destruction (greater than 98%) is achievable using excess oxidant and temperatures of 600 °C (1,112 °F) [13]. Other studies have shown, however, because of the single-phase conditions that promote complete mixing in the reactor, the effects of oxidant in excess of the stoichiometric requirement on the overall reaction were negligible and the use of an oxidant source at slightly above the stoichiometric demand may be sufficient [20]. Additionally, optimization of a mobile, 0.5 gpm unit indicated that operating at a 10% excess stoichiometric oxidant requirement is adequate [29].

SCWO conditions may also be used to reduce compounds by reaction with a readily oxidizable compound. In these cases, no oxygen source is added to the process. Nitrate

reduction with methanol, ammonium or ferrocyanides as a reductive source, was shown to take place very rapidly and achieve greater than 99.9% destruction [18]. The reduction of ammonia using ethanol as an auxiliary fuel has also been demonstrated to be effective [30].

Air, oxygen, or hydrogen peroxide are the primary oxidants used in SCWO processing. A comparison of the effectiveness of oxygen and hydrogen peroxide indicated that hydrogen peroxide was more effective in the subcritical temperature range (200 ° - 300 °C [392 ° - 572 °F]) whereas oxygen was more effective at supercritical temperatures (400 ° - 500 °C [752 ° to 932 °F]) [17]. Selection of the oxidant to be used is also dependent upon economics. Hydrogen peroxide is the most expensive oxidant with costs considerably higher than those for oxygen and economics may dictate the use of oxygen or air. The use of pure oxygen over air offers the advantage of not introducing high levels of nitrogen into the system which adds to the volume of throughput without providing any benefits to the system. In fact, large amounts of nitrogen introduced into the system could lead to undesirable products in the gas effluent.

The SCWO process can achieve almost total destruction of all oxidizable organic compounds [21]. The amount of destruction achieved is dependent upon the pressure, temperature, and residence times in the reactor. Of these three parameters, temperature appears to have the most effect on the rate of reaction and destruction efficiency, while pressure has very little effect on the rate of reaction once supercritical conditions are achieved. Therefore, the pressure should be kept as low as possible to minimize the cost of the reactor because increased pressure requires much thicker reactor walls and thus higher material costs [20]. The following carbon conversion efficiencies are reported to occur [21].

- 99 to 99.9% at 400-500 °C and 1 to 5 minutes residence time
- Up to 99.9% at 500-550 °C with 1 minute residence time
- 99.999% at 550-600 °C and less than 1 minute residence time
- Greater than 99.9999% at 600-650 °C with a residence time of seconds

Table 3-1 contains a list of compounds treated by SCWO and the corresponding treatment conditions and destruction efficiencies [12]. As can be seen from the table, successful

Table 3-1

Chemicals Successfully Treated by Supercritical Water Oxidation and Typical Destruction Efficiencies[a]

Organic Compound	Bench-Scale	Pilot-Scale	Destruction Efficiency[b] (%)
Acetic Acid	x		
Acetylsalicylic Acid (Aspirin)	x		
Ammonia		x	>99.71
Aroclors (PCBs)	x	x	>99.995[c]
Benzene	x		
Biphenyl	x		99.97
Butanol	x		
Carbon Tetrachloride		x	>96.53[c]
Carboxylic Acids	x		
Carboxymethyl Cellulose	x		
Cellulose	x		
Chlorinated Dibenzo-p-dioxins	x		>99.9999
Chlorobenzene		x	
Chloroform		x	>98.83[c]
2-Chlorophenol		x	>99.997[c]
o-Chlorotoluene	x	x	>99.998[c]
Cyanide		x	
Cyclohexane	x		99.97
DDT	x		99.997
Decachlorobiphenyl	x		
Dextrose	x		99.6
Dibenzofurans	x		
3,5-Dibromo-N-cyclohexyl-N-methyltoluene-α,2-diamine	x		
Dibutyl Phosphate	x		
Dichloroacetic Acid	x		
Dichloroanisole	x		
Dichlorobenzene	x		
4,4'-Dichlorobiphenyl	x		99.993

Table 3-1

Chemicals Successfully Treated by Supercritical Water Oxidation and Typical Destruction Efficiencies[a]
(Continued)

Organic Compound	Bench-Scale	Pilot-Scale	Destruction Efficiency[b] (%)
1,2-Dichloroethylene	x		99.99
Dichlorophenol	x		
Dimethyl Sulfoxide		x	
Dimethylformamide		x	
4,6-Dinitro-o-cresol	x		
2,4-Dinitrotoluene	x		99.9998
Dipyridamole	x		
Ethanol	x		
Ethyl Acetate		x	
Ethylene Chlorohydrin	x		
Ethylene Glycol	x		>99.9998[c]
Ethylenediamine Tetraacetic Acid	x		
Fluorescein	x	x	>99.9992[c]
Hexachlorobenzene	x		
Hexachlorocyclohexane	x	x	>99.9993[c]
Hexachlorocyclopentadiene	x		99.99
Isooctane	x		
Isopropanol	x	x	
Mercaptans	x		
Methanol	x	x	
Methyl Cellosolve	x		
Methylene Chloride	x	x	
Methyl Ethyl Ketone	x		99.993
Nitrobenzene		x	>99.998[c]
2-Nitrophenol	x		
4-Nitrophenol	x		
Nitrotoluene	x		
Octachlorostyrene	x		

Table 3-1

Chemicals Successfully Treated by Supercritical Water Oxidation and Typical Destruction Efficiencies[a]
(Continued)

Organic Compound	Bench-Scale	Pilot-Scale	Destruction Efficiency[b] (%)
Octadecanoic Acid Magnesium Salt	x		
Pentachlorobenzene	x		
Pentachlorobenzonitrile	x		
Pentachloropyridine	x		
Phenol	x		
Sodium Hexanoate	x		
Sodium Propionate	x		
Sucrose	x		
Tetrachlorobenzene	x		
Tetrachloroethylene	x	x	99.99
Tetrapropylene H	x		
Toluene	x		
Tributyl Phosphate	x		
Trichlorobenzenes	x		99.99
1,1,1-Trichloroethane	x	x	>99.99997[c]
1,1,2-Trichloroethane		x	>99.981[c]
Trichloroethylene	x		
Trichlorophenol	x		
Triflouroacetic Acid	x		
1,3,7-Trimethylxanthine	x		
Urea	x		
o-Xylene	x		99.93

[a]Source: "Supercritical Water Oxidation Technology: A Review of Process Development and Fundamental Research."[12]

[b]No entry for destruction efficiency indicates that a quantitative determination was not reported.

[c]Compound undetectable in effluent; quoted efficiency is based on analytical detection limit.

SCWO of a broad range of compounds has been achieved. No toxic products were reported as a result of this destruction.

3.2.4 Treatment System Effluent

The oxidation reactions result in essentially complete destruction of hazardous organic compounds. Given sufficient temperature, pressure and residence time, the oxidation reactions will go to completion and the effluent from the process will contain water; gas consisting of CO_2, oxygen (O_2), and molecular nitrogen (N_2) if nitrogen is present in the feed such as when air is used as the oxidant; metals previously present in the feed, which are completely oxidized to form metals oxides [31]; and inorganic mineral acids or neutralized salts if the waste contains sulfur, halogens, or phosphorous. The valence state of metals in the waste influent may be changed during the SCWO process. For instance, Cr^{+3} is oxidized to Cr^{+6} during SCWO treatment [31a]. The gas contains no NO_x, no acid gases (sulfur dioxide, hydrochloric acid), no particulate matter and less than 10 ppm carbon monoxide [32].

Carbon dioxide (CO_2) is the primary reaction product formed from carbon conversion in SCWO. The CO_2 is easily separated into the gas phase when the effluent is cooled and depressurized because the solubility of the CO_2 is greatly reduced at ambient conditions. The CO_2 is either vented directly to the atmosphere if the process results in complete oxidation, or air pollution control equipment may be used as a safety precaution if the compounds being oxidized are extraordinarily hazardous or if incomplete oxidation may occur. Other carbon compounds present in the effluents are carbon monoxide and inorganic and organic compounds (CO_3^{2-} and HCO_3^-). Carbon monoxide may be present at less than 10 ppm [30, 32]. Tests conducted at Los Alamos on SCWO of rocket fuels and explosives indicated inorganic carbon compounds present in the aqueous effluent streams in quantities of less than 8 ppm.

For nitrogen-containing compounds, nitrogen gas is the predominant end product from complete oxidation regardless of the oxidation state of the nitrogen in the initial waste

stream, with small amounts of nitrous oxide (N_2O) also formed [30]. Because of concerns with the formation of ammonia which appears to be the rate-controlling intermediate for oxidation of nitrogen-containing compounds [33] and which is difficult to treat using SCWO, and NO_x as byproducts of the oxidation, the formation of these compounds has been investigated through the oxidation of ammonia to N_2 and N_2O [30]. The oxidation of ammonia, using urea as the feedstock because it readily decomposes to CO_2 and ammonia, was demonstrated to increase with increasing temperatures. The highest destruction efficiency for urea was reported to be 41% at 690 °C (1,274 °F). Much higher destruction efficiencies (greater than 90%) were reported at lower temperatures using ethanol as a supplementary fuel, thus demonstrating the beneficial effects of co-oxidation with a more easily oxidized compound [30]. With regard to NO_x, both inorganic and organic nitrogen compounds are reduced to nitrogen in the SCWO, with gas phase NO_x being below 1 ppm, while N_2O was 400 ppm [30]. The NO_x is scrubbed from the air stream by the water in the system and reacts to form nitric acid and nitrous oxide [30]. Kinetic studies of nitrate and nitrite ions with various reducing agents or a minimum of excess oxidant present in the SCW show that they can be rapidly and completely destroyed at temperatures above 525 °C (977 °F) [27].

Inorganic acids are formed as a result of the oxidation of sulfur, halogens, or phosphorous compounds present in the feed stream. The formation of the acids can create corrosion problems in the reactor and piping if the pH drops below 2 [23]. To prevent corrosion problems, the acids are neutralized as they are produced to form inorganic salts by adding caustic solutions of sodium hydroxide or calcium hydroxide to the feed stream [28, 25, 23]. However, the inorganic salts form precipitates because of their low solubilities at supercritical conditions [32, 23]. The precipitated salts must be separated from the supercritical fluid to prevent buildup of salts in the system and plugging of the piping.

The formation of the acid salts in the system has turned out to be the most significant design problem. The salts formed are "sticky" and adhere to the walls and surfaces of the equipment, thus requiring special reactor designs or frequent and costly shutdowns to flush the reactors in order to remove the salts. Modar has reportedly developed a reactor in

which the supercritical water is present above a bath of water at subcritical conditions [17, 23]. A schematic of this reactor is shown in Figure 3-4. The precipitated materials settle out of the supercritical water and pass into the subcritical water where they are re-solubilized and transported out of the reactor. Pilot tests conducted using this reactor indicated that the brine letdown and filter system have been effective in preventing the plugging of downstream equipment [23]. A second solution to the salt problem is to not neutralize the acids in the reactor, but to let the acidic solution pass out of the reactor where it can then be neutralized under ambient conditions. This requires additional development of corrosion resistant materials, such as titanium alloy, gold, or ceramic reactor and piping systems [23].

Research conducted at the University of Texas indicates that a pressure vessel acting as a salt separator achieved removal of sodium sulfate and sodium chloride salts to near their solubility limits in SCW, while sodium nitrate was removed at greater than 96% efficiency at a temperature of 550 °C (1, 022 °F) and a pressure of 34.4 MPa (4,989 psi) [34]. The feed wastes were simulated to represent the wastes contained in underground storage tanks at the Department of Energy site in Hanford, Washington. These wastes consist largely of sodium salts.

3.2.5 Reaction Kinetics

Much research has been conducted on the reaction kinetics of SCWO, although additional data are required on many compounds such as chemical agents and energetic materials [33]. Various kinetic data for different wastes are compiled in Table 3-2. The data in this table apply to the generalized kinetic form $-\dfrac{dc}{dt} = k[c]^m [0]^n$ and $k = k^\circ \exp [-Ea/RT]$ where [C] and [O] are the concentrations of organic reactant and oxidant respectively; Ea is the activation energy (KJ/mol), T is in degrees Kelvin, and $R = 8.314$KJ/mol-K. This table was compiled from several sources [33, 35]. These data exhibit three general trends. First, the oxidation rate is independent or weakly dependent upon the oxidant concentration. Next, SCWO reactions follow approximate first-order reaction kinetics with respect to the concentration of the starting compounds and zero order kinetics with respect to the oxidant.

Table 3-2

Kinetic Models for Supercritical Water Oxidation of Organic Substances

Compounds	Oxidant	Reactor Type	Kinetic Parameters*				Temperature (K)	Pressure (atm)	$[C_A]_o$ (g/L)	References
			k	Ea	m	n				
Acetamide	H_2O_2	Flow	2.75×10^3	88.3	1.15	0.05	673-803	240-350	1.5-4.0	Lee, 1990
Acetamide**	H_2O_2	Flow	5.01×10^4	94.7	1	0.17	673-803	240-350	1.5-4.0	Lee, 1990
Acetic Acid	H_2O_2	Flow	2.63×10^{10}	167.1	1	0	673-803	240-350	1.3-3.3	Lee, 1990
Acetic Acid	H_2O_2	Flow	9.23×10^7	131	1	0	673-773	240-350	1.0-5.0	Wilmanns, 1990
Acetic Acid	O_2	Flow	9.82×10^{17}	231	1	1	611-718	394-438	0.525	Wightman, 1981
Acetic Acid	O_2	Flow	2.55×10^{11}	172.7	1	0	611-718	394-438	0.525	Wightman, 1981
Activated Sludge (COD)	O_2	Batch	$\sim 1.5 \times 10^2$	~54	1	0	573-723	240-350	46.5	Shanableh, 1990
Ammonia	O_2	Flow	3.16×10^6	157	1	0	913-973	246	0.03-0.11	Webley et al., 1991
2-Butanone	O_2	Batch	1.20×10^1	36.2	1	0	673-773	240-400	~6	Griffith and Gloyna, 1992
Carbon Monoxide	O_2	Flow	3.16×10^6	112	1	0	673-814	246	0.02-0.11	Helling and Tester, 1987
Carbon Monoxide**	O_2	Flow	3.16×10^9	134	0.96	0.34	693-844	246	0.01-0.98	Holgate et al., 1992
o-Cresol	O_2	Batch	3.16×10^0	28.5	1	0	673-773	240-400	~10	Griffith and Gloyna, 1992
Digested Sludge (COD)	O_2	Batch	4.36×10^3	20.4	1.86	0.38	573-723	240-350	46.5	Tongdhamachart, 1990
2,4-Dichlorophenol	O_2	Flow	1.92×10^4	71.9	1	0	683-788	276	0.4-0.8	Crain and Gloyna, 1992
Ethanol	O_2	Flow	6.46×10^{21}	340	1	0	755-814	241	.03-.036	Helling, 1986

Table 3-2

Kinetic Models for Supercritical Water Oxidation of Organic Substances
(Continued)

Compounds	Oxidant	Reactor Type	Kinetic Parameters*				Temperature (K)	Pressure (atm)	$[C_A]_o$ (g/L)	References
			k	Ea	m	n				
Formic Acid	O_2	Flow	-	~96	1	1	683-691	408-432	1.0	Whightman, 1981
Glucose (TOC)	-	Batch	-	130	0.5	1	653-683	~400	~10	Whitlock, 1978
Methane	O_2	Flow	1.26×10^7	156.8	1	0	913-973	245	-	Rofer & Streit, 1989
Methane	O_2	Flow	2.51×10^{11}	178.9	0.99	0.66	833-903	245	-	Webley and Tester, 1991
Methane	O_2	Flow	2.04×10^7	141.7	1	0	833-903	245	-	Webley and Tester, 1991
Methanol	O_2	Flow	2.51×10^{24}	395.0	1	0	723-823	243	-	Rofer & Streit, 1989
Methanol	O_2	Flow	3.16×10^{26}	408.1	1.1	-0.02	723-823	243	0.038-0.17	Webley et al, 1990
Phenol	O_2	Flow	2.61×10^3	63.8	1	1	557-702	292-340	0.1-0.4	Wightman, 1981
Phenol	O_2	Flow	-	-	0.5	0	653	188-778	0.25-1.0	Thornton and Savage, 1990
Pyridine	O_2	Flow	3.44×10^1	227	1	0.2	698-800	276	1-3	Crain and Gloyna, 1992

* Kinetic parameters are defined by $-d[C]/dt = k[C]^m[O]^n$ and $k = k^o exp(-E_a/RT)$, where [C] and [O] are concentrations of organic reactants and oxidant, respectively; E_a is in kJ/mol; T is in K; R = 8.314 J/mol-K; and k^o = 1/sec (first-order), etc. - Not available. $[Ca]_o$ = feed concentration. The concentration of compounds labeled with COD is quantified by chemical oxygen demand method; and concentration of other compounds is quantified by chromatographic techniques. The excess oxidants are used in all tests. Kinetic parameters are reported for the overall reaction in water unless otherwise indicated.

** Parameters have been obtained for oxidation only (i.e., excluding reactions with water).

Source: "Supercritical Water Oxidation: An Engineering Update."

Third, the activation energy (that is, minimum energy required for a reaction to occur) ranges from about 30 kJ/mol to 480 kJ/mol [33, 17]. Very little work investigating the use of catalysts, additives, and alternative oxidants has been performed [31]. The wide variation in kinetic parameters seen in Table 3-2 indicates that kinetic data would need to be developed for previously untested materials prior to the design of a SCWO unit because a generalized model is not widely applicable.

Studies have shown that the major oxidation intermediates (under wet air oxidation subcritical conditions) are: 1) acetic acid for hydrocarbons and oxygenated hydrocarbons, 2) ammonia for nitrogen-containing organics, and 3) chloromethane for chlorinated organics. These rate-controlling intermediates must be further oxidized to have complete destruction. The acetic acid is readily oxidized at supercritical temperatures [11] whereas ammonia requires a co-oxidant as noted in Section 3.2.4.

3.2.6 Advantages/Disadvantages of the SCWO Technology

SCWO has numerous potential advantages as a treatment technology for highly hazardous substances. The principal advantages are:

- SCWO takes place in a totally enclosed treatment system which is designed under normal operation to prevent releases of contaminants to the environment. Any compounds that are not oxidized will be contained in the liquid effluent from the reactor, which may be sampled prior to discharge.

- SCWO has limited emissions of hazardous substances. The primary products formed are water, carbon dioxide, nitrogen and inorganic acid salts. Minor byproducts may include ammonia, nitrous oxide, carbon monoxide, and nitrogen oxides. These compounds would be present in the low ppm range.

- As shown in Table 3-1, SCWO is capable of achieving high destruction efficiencies. Destruction efficiencies of greater than 99.9999% have been noted [23].

- SCWO does not form other hazardous pollutants such as NO_x (NO_x not formed at temperatures up to 700 °C [1,292 °F]), acid gases, or particulate matter in the gaseous effluent [21].

While SCWO has numerous advantages, it also has several disadvantages which are the principal areas of current research. These problems have to do primarily with ensuring long-term treatment system reliability and issues regarding scale-up of the process to full scale. The primary problems are associated with ensuring long-term system reliability related to scaling and corrosion. The issue of solids separation has reportedly been solved by the development of an innovative salt/solids separation technology developed by MODAR, Inc. [23]

Corrosion of the reactor is a major problem and the need to create a less corrosive environment inside the reactor is one of the major areas of current research [36]. Corrosion testing conducted at Sandia National Laboratories using witness wires of Inconel 625, Hastelloy C-276 and titanium placed inside a SCWO reactor exhibited severe selective dissolution of chromium, nickel, and molybdenum for some conditions, and non-selective dissolution for other conditions [36]. Testing at the University of Texas on Hastelloy C-276 indicated that corrosion using an oxidant (nitrate or hydrogen peroxide) selectively dissolved chromium from the matrix, whereas corrosion was non-selective when no oxidant was used [36]. The dissolution of metals from the process equipment will affect the ultimate discharge of the treated water because the metals content in the discharge may exceed standards and require further treatment for metals removal. Reactors being used in treatability and pilot work include gold-lined reactors [13], rhodium-titanium and iridium-titanium reactors [31], Incalloy 625, Hastelloy C-276 [37]. An optically accessible reactor was developed by Sandia National Laboratory for materials research purposes which allows for the use of laser-based diagnostics to probe the reacting flow [37]. The University of Texas is also experimenting with ceramic materials for use in reactor construction [8]. Other attempts at reducing the corrosion include the addition of neutralization agents to the reactor to precipitate the corrosive chlorides (sodium chloride is only slightly soluble in supercritical water). When stainless steel or titanium reactors are used in the presence of chloride ions, the potential also exists for stress corrosion cracking. Stress corrosion cracking occurs along the metal's grain boundaries in the presence of chloride. As the name implies, this phenomenon occurs only when the metal is under stress. The high pressures used in SCWO processing impose stress on the reactor walls. Thus, for waste streams

containing chlorides, stainless steel and titanium reactors may be subject to stress corrosion cracking.

Another design obstacle for SCWO is the formation of hydrothermal flames when oxygen is injected into the SCWO reactor in the presence of methane or methanol. These flames can cause damage to the reactor and also create NO_x as a result of localized high temperatures [38].

Finally, SCWO technology has been demonstrated only at the bench- and pilot-scale. To date, no full-scale SCWO units have been developed. As such, there is limited available information pertaining to scaling up of equipment. Furthermore, limited information is available concerning long-term system reliability.

In evaluating the potential advantages and disadvantages of SCWO processing, SCWO must be compared to the more established technology of incineration. This comparison may be made based on the following points:

- Although destruction efficiency is somewhat waste specific, waste destruction is generally comparable for incineration and SCWO technologies. The performance standard for incinerators listed in 40 CFR 264.343 is 99.99% destruction of all feed constituents. This destruction efficiency has been reported by SCWO for a variety of organic compounds.

- If batch processing is used, SCWO would be capable of destroying contaminants from many inorganic surfaces without destroying the carrier material. Because of the higher operating temperatures used in incineration, it is unlikely that many carrier materials could withstand the process.

- SCWO processing does not generate NO_x, acid gases, or particulate matter commonly produced during incineration. [21]

- Materials handling issues and safety precautions would likely be similar for SCWO and incineration processing. SCWO processing is usually conducted continuously, however, requiring solid materials to be solubilized or slurried prior to treatment. This pretreatment step for solids is not required for incineration.

- Incineration has been documented to be reliable and available at the field-scale. Although SCWO processing may be equally reliable, it has not yet been widely proven.

- Although it is commonly felt that SCWO processing will receive wider public acceptance than incineration and thus permittability will be easier than that for incineration, incineration has repeatedly been demonstrated to be a permittable process.

- An economic evaluation of SCWO technology versus incineration for specific waste scenarios is given in Subsection 4.2.9. The costs of incineration are much more firmly established and widely accepted than those for SCWO processing.

- Materials of construction are still an area of research for SCWO processing. Although the materials used to construct incinerator units are well established, operational constraints are imposed by the properties of the incinerator refractory ceramic lining.

3.3 EXTRACTION PROCESSES

The following subsections contain a general discussion of typical extraction processes, primarily for SFE, that are used to separate contaminants of concern from various media as well as for other applications. The discussion will include a brief introduction to the technology followed by a general process description, process parameters that affect the technology, waste applicability or identification and handling of process streams, limitations and advantages of the technology, status and general cost effectiveness considerations and finally a brief summary discussing the appropriateness of the extraction technology. The primary focus of this subsection is on SFE and accordingly only SFE is discussed in detail while other solvent extraction processes (conducted at subcritical or even ambient temperatures) are limited in discussion to the extent that they provide a general process discussion and their current applications for comparison with SFE.

3.3.1 Background

In comparison with conventional processes, SFE offers considerable flexibility for an extractive separation using the variables of pressure (P), temperature (T), choice of solvent,

and additives called "entrainers" or "modifiers." Heavy non-volatile substances dissolve in supercritical fluids typically 2 to 7 orders of magnitude in excess of the amount predicted by the ideal gas law. This phenomenon is due to the high density of the fluid in the supercritical state, which can approach that of a liquid. Thus SFE offers both high solubility extraction based on the enhancement of vapor pressure, and nearly complete solvent-extract separation, accomplished by reducing the solvent density to the gaseous state [39].

A major application of SCFs is in the petroleum industry in which a Residuum Oil Supercritical Extraction Process (ROSE) was developed by Kerr-McGee Refining Corporation (Kerr McGee) [40, 41, 42].

SFE has also found applications in the treatment of hazardous wastes as well as extracting valuable products in the food and pharmaceutical industries. Extraction of pesticides and PCBs from soils has been demonstrated at the bench scale.

3.3.2 Process Description

Figures 3-5 and 3-6 are schematic drawings of typical SFE processes for treatment of contaminated aqueous and soil media, respectively [43]. The reactor is generally run in a continuous, countercurrent fashion for aqueous wastes. For solid wastes, however, batch processes are generally preferred because of the difficulties associated with transferring solid material into a pressurized vessel. Figure 3-5 shows a continuous extractor for use with aqueous waste.

The extracting fluid chosen for this example is CO_2, although other fluids would be treated in a similar manner. Liquid wastes enter at the top of the vessel and supercritical CO_2 is introduced at the bottom, flowing countercurrently to the waste. Supercritical conditions are maintained within the reactor. As the CO_2 contacts the waste, organics are extracted. Organic-laden CO_2 is then removed from the top of the column, while the treated waste exits at the bottom. The CO_2/extract stream then is separated by lowering the system pressure. Depending on the compound properties, the pressure can either be lowered
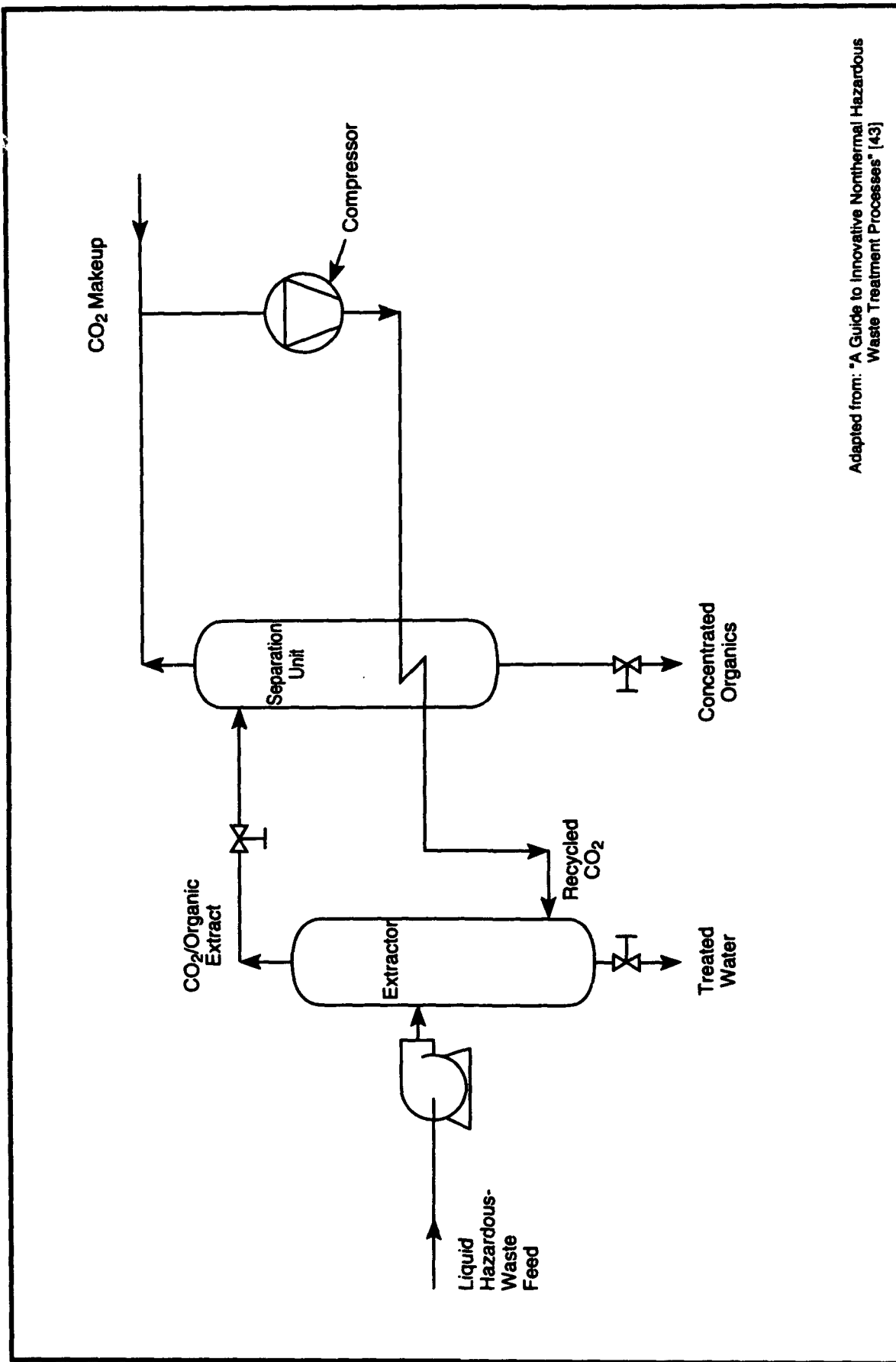
FIGURE 3-5 TYPICAL SFE PROCESS FOR TREATMENT OF AQUEOUS MEDIA

Adapted from: "A Guide to Innovative Nonthermal Hazardous Waste Treatment Processes" [43]

94P-1488 3/9/94
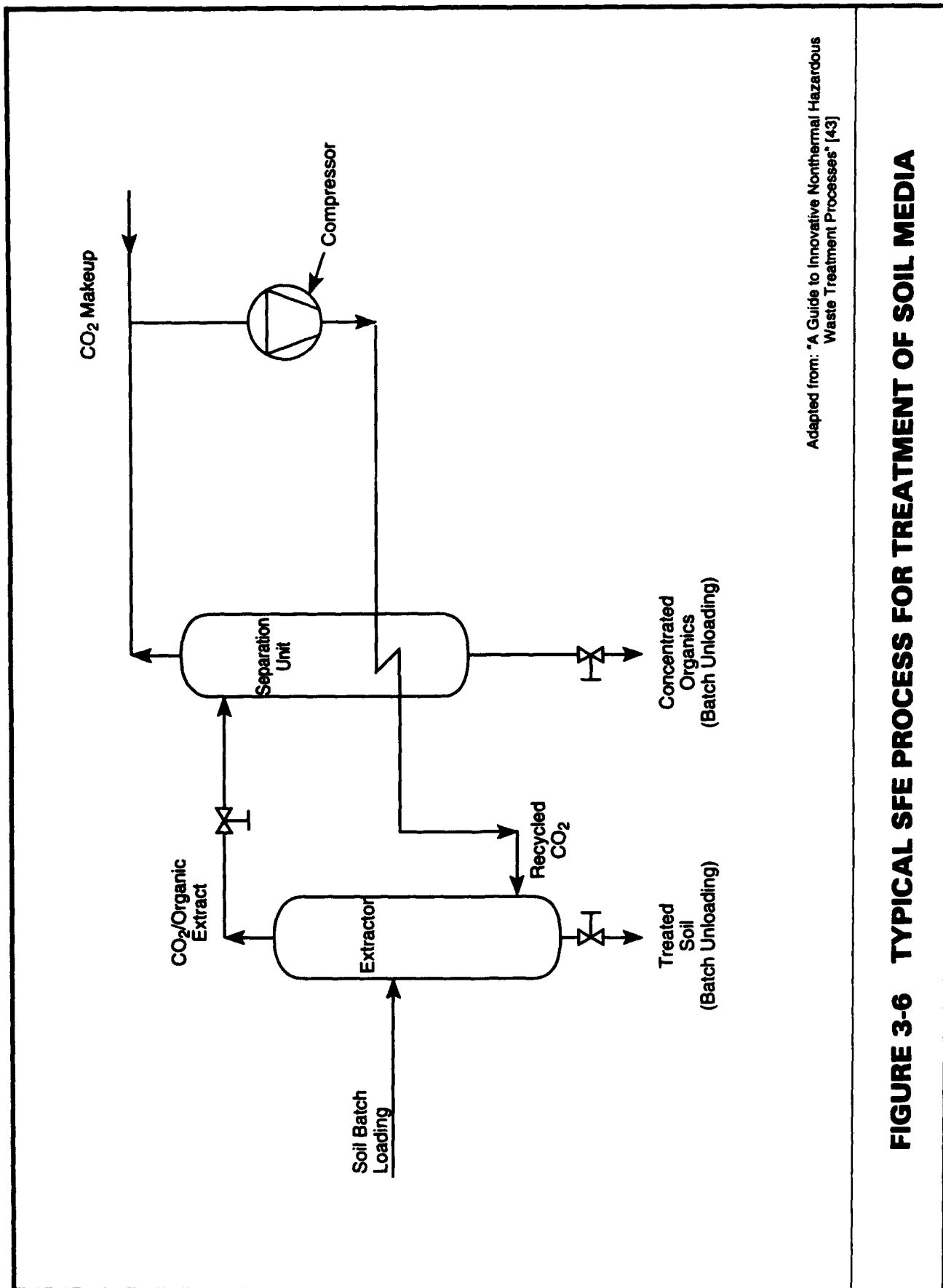
FIGURE 3-6 TYPICAL SFE PROCESS FOR TREATMENT OF SOIL MEDIA

Adapted from: "A Guide to Innovative Nonthermal Hazardous Waste Treatment Processes" [43]

94P-1489 3/9/94

enough to vaporize the CO_2, leaving behind only the liquid stream or lowered to a subcritical point where CO_2 is liquified and can be separated from the extract by distillation. In either case, the separated CO_2, along with any needed makeup CO_2, is recompressed and recycled to the reactor [43].

Figure 3-6 is a typical soil media extraction unit. Soil processing differs from aqueous processing in that it is normally conducted in a batch-mode because of the difficulties in pumping solids into a pressurized vessel, and it requires potentially long contact times as a result of mass transfer limitations. Soil is charged into a reactor which is then pressurized. Supercritical CO_2 is introduced in the bottom of the reactor, and then flows upward through the soil and extracts contaminants. After exiting the reactor, the CO_2 is vaporized as a result of reduced pressure, and leaves the liquid extract. The CO_2 is then recompressed for recycle.

3.3.3 Factors Affecting SFE Process Efficiency

Several factors affect the SFE process. These operating parameters/factors have been studied to a great extent by several researchers as is discussed in the following paragraphs. The most critical parameters that affect SFE include the choice of the SCF and its critical temperature (T_c) and critical pressure (P_c), the process operating temperature (T) and pressure (P), the addition of entrainers or modifiers to enhance the extraction process, and other mass transfer characteristics of the SCF.

Favorable mass transport characteristics of SCFs make them ideal extraction solvents [56]. Solubilities in supercritical CO_2 are typically strong functions of pressure (and thus CO_2 molar concentration), especially near and around the critical temperature and pressure. Up to several orders of magnitude change in solubility can be produced by moderate pressure variations near the critical point. While solubility tends to increase as pressure increases, solubility may decrease with temperature in the range from the critical pressure to twice the critical pressure because of a combination of fluid density and thermal effects on solubility.

The density of an SCF is more sensitive to temperature near the critical pressure than at higher pressures. At these near-critical pressures, this density decrease with increasing temperatures dominates the effect on vapor pressure. At the higher pressures, the dominant temperature effect is on the vapor pressure. In addition to the density, the viscosity and diffusivity for typical SCFs are intermediate between those of a liquid and a gas. While an SCF has a density approaching that of a liquid with high solvent capacity, the diffusivity is orders of magnitude greater, giving improved mass transfer rates. For these reasons, supercritical solvents are superior to typical liquid solvents for penetrating the micropores of a solid structure such as coal [39]. In addition, the lower viscosity also provides advantages such as enhanced solids settling rates during precipitation.

Although the benefits of dramatic changes in the density of a fluid near the critical point are being exploited in problems concerning phase equilibria, the potential for similar benefits in chemical kinetics is relatively unknown. Small changes in temperature or pressure in the critical region can lead to large changes in the rate constant or rate of reaction. The latter results from large changes in the concentration of a reactant, product, or catalyst in the supercritical phase [45]. As was shown in Figure 3-2, near the critical point, small changes in temperature result in large property changes. Changes in this region are much more dramatic than at ambient conditions.

3.3.4 Applicability of SFE

3.3.4.1 Treatment of Toxic/Hazardous Wastes

Certain gases (e.g., carbon dioxide) become excellent solvents for organic compounds when they are maintained at or above their critical temperature and pressure. This concept is being used to develop technologies for the extraction of organics from hazardous wastes and contaminated soils. Critical Fluid Systems, Inc. (CFS), a subsidiary of Arthur D. Little, Inc., has commercialized an SFE process for treating liquid, semi-solid, and solid hazardous wastes. Extractions have been conducted using supercritical CO_2 and subcritical propane. Some of the organics that, in the opinion of CFS, are candidates for treatment using this

technology are listed in Table 3-3. According to CFS, final concentrations as low as 100 ppb may be obtained at capacities from 5 to 100 gpm. (Initial concentrations were not reported [43].) Removal of 90% of the PCBs from spiked soil samples has been reported with a residence time of less than 10 minutes [43]. Also, a 90% PCB extraction efficiency was demonstrated by CFS in a Superfund Innovative Technology Evaluation (SITE) program. Although the solvents used for this demonstration, liquified propane and butane, were maintained in the subcritical state, the equipment and process used were similar to supercritical extraction techniques [44]. CFS is in fact focusing much of its current extraction research on the use of subcritical liquified propane because of the lesser energy demands of a subcritical process [45].

Supercritical CO_2 has been used to extract PCBs, DDT, and toxaphene from contaminated soil at the bench-scale. Since the solubility of DDT in CO_2 is negligible, methanol was added to increase the contaminant solubility, thus increasing extraction efficiency [46]. Methanol in this situation is known as a modifier. By increasing the contaminant solubility, the modifier decreases mass transfer resistance and facilitates reaction. Supercritical CO_2 containing 5% methanol by weight at a flowrate of 0.7 g/s demonstrated leaching of 95% of the DDT from soil with a residence time of less than 5 minutes as compared to a 70% removal demonstrated without the modifier. In both cases, the soil had an initial concentration of 1,000 ppm. The same extraction mixture was applied to a soil containing the PCBs 3,500 ppm Aroclor 1260 and 2,100 ppm Aroclor 1242. Over 98% extraction of the contaminants was realized in 10 minutes. Approximately 75% of the toxaphene (a chlorinated pesticide) was leached in under 10 minutes without the use of a methanol modifier. Studies have also been conducted at Louisiana State University in which the extract is catalytically oxidized to destruction. To date, only partial oxidation has been demonstrated [46].

CFS concluded that supercritical CO_2 extraction was economically advantageous for the regeneration of activated carbon which had been used for adsorption of pesticides or other

Table 3-3

Representative Organics Candidates for Treatment with SFE

Acetone	Methylene chloride
Benzene	Methyl ethyl ketone
Butanol	Methyl methacrylate
Butyric acid	Naphthalene
Carbon tetrachloride	Nitrobenzene
Chlorobenzene	Oils and grease
Chloroform	Pentachlorophenol
1,1-Dichloroethane	Phenol
1,2-Dichloroethane	Propanol
Ethylbenzene	Propionic acid
Furfural	Trichloroethane
Gasoline	Trichloroethylene
Heptane	Toluene
Ketones	Vinyl acetate
Methyl acetate	Xylene

Source: Critical Fluid Systems, Inc. [45]

pollutants in wastewater treatment. The conventional thermal regeneration process that uses a reforming atmosphere of combustion gases and steam at about 930 °C (1,700 °F) is capital and energy intensive, and gives off corrosive gases [45].

SFE methods have been developed for the extraction of petroleum-related products from soils and sludges. Contaminants studied have included gasoline-, diesel-, and crude oil-range hydrocarbons, polynuclear aromatic hydrocarbons (PAHs), and ionic surfactants. Extraction with supercritical CO_2 at 150 °C (302 °F) has been shown to remove even heavy hydrocarbons from soil and sludges. PAH recovery was shown to be most effective with supercritical freon, which is difluorochloromethane ($CHClF_2$) [48]. A coal tar contaminated soil containing more than 0.1% PAH was also treated by supercritical fluid extraction with carbon dioxide using a methanol modifier. Operating conditions were 50 °C (122 °F) and 350 atm (5,145 psi) with a retention time of 3 to 7 hours [49]. Addition of methanol and water as polar modifiers increased PAH solubility in supercritical CO_2 during extraction from contaminated soil. The polar modifier addition had the further benefit of displacing PAH molecules at polar adsorption sites on the soil [9].

3.3.4.2 Upgrading Heavy Residuals and Heavy Oils - Petroleum Industry/Coal Processing Industry and Fuel Development

An energy-efficient ROSE process was developed for upgrading heavy crudes and residuals [40, 41, 42]. Although the ROSE process has not been applied to environmental wastes, it does present an example of a commercial-scale SFE application and thus will be described. The ROSE process is being used to produce feedstocks for catalytic cracking, hydrocracking, lube oils, asphalts, and many other specialty products using appropriate SCFs. The development of this process was stimulated by the need to reduce raw material requirements and to conserve energy. Additionally, the potential exists for recovering more valuable products from the heavy non-distillate portion of a barrel of crude oil.

The ROSE process takes advantage of the phenomenon of reverse solubility (reduced solubility of the oil in the solvent with increased temperature), coupled with the difference in density between the oil and the solvent or solvent-oil solution to effect a separation

between two fluid phases [41]. The energy required by ROSE solvent recovery is substantially lower than that required by any other method including conventional evaporation. Not only is the heat of vaporization eliminated, but so is the energy needed for compression of the vaporized solvent. Furthermore, a major portion of the energy required to achieve supercritical temperature of the solvent is recoverable through counter-current heat exchange within the system.

As indicated previously, the first commercial-scale ROSE process plant was constructed by Kerr-McGee in 1954 [40]. This plant operated successfully over a six-year period processing feedstocks ranging from 85-100% asphalt to a topped crude with only the naphtha fraction removed. Since then, the ROSE process has been used by domestic refiners to produce a wide spectrum of products, as well as incremental feedstocks for other downstream processes such as catalytic cracking and hydrocracking, and specialty products. The ROSE process has also been combined with thermal cracking and hydro-treating for high conversion of heavy oils into upgraded products. Bench-scale ROSE pilot-plant facilities are available at Kerr-McGee's Technical Center in Oklahoma City, OK, to evaluate feedstocks for potential licensees as well as to set the design basis for commercial ROSE units.

3.3.4.3 Cleaning Metal Substrates

Liquid/supercritical fluid carbon dioxide has been applied as an alternative to halocarbon solvents, such as the widely used freon, that are conventionally used for washing organic and inorganic contaminants from the surface of metal parts and machining fines [50]. This process has potential applicability for cleaning or decontaminating parts at various Army installations. This cleaning process was demonstrated at Rocky Flats Laboratories on a bench-scale for steel and uranium substrates and was found compatible with plutonium (plutonium undergoes repeated in-process contacts with various organic substances during fabrication and assembly of weapons components). The efficiency of this process depends on the process temperature, pressure, and fluid flow rates as well as cleaning time. Moderate fluid flow rates produced acceptable degreasing results in less than 10 minutes using a simple flow-through process configuration operating at pressures greater than 175

atm (2,540 psia) and temperatures greater than 40 °C (104 °F). The cleaning efficiency was found to increase by increasing pressure and flow rate within the parameter range studied. This process was also used to remove more than 99.5% of the light hydraulic oil from steel fines. CO_2 was selected as the cleaning agent (at supercritical conditions) for removing oils and other substances that adhere to the plutonium parts during machining and forming, because it is naturally occurring, environmentally safe, nontoxic, inexpensive, and nonflammable. [50]

3.3.4.5 Food and Pharmaceutical Applications

SCF technologies are widely used in the pharmaceutical and food industries [51]. CO_2 is used commercially to extract caffeine from coffee in a German plant processing 60,000,000 pounds per year of green coffee [51]. Additionally, dry CO_2 is routinely used to extract the aroma and flavor oils from roasted coffee beans. The bitter alpha-acids, which give beer its characteristic flavor, are commercially extracted from hops using CO_2. Similar processes under development include extractions of various types of pepper, nutmeg, soybeans, and corn. CO_2 is also used to extract vegetable oils from various beans at much lower pressures than conventional solvents. Using a micro-analytical technique, it has been demonstrated that compounds including limonene, menthol, caffeine, and triglycerides can be extracted from plant materials such as caraway fruits, peppermint leaves, camomile flowers, sunflower seeds, raw coffee, and sesame seeds using CO_2. Supercritical CO_2 can also be used to extract cholesterol from milk, butter, cheese, beef tallow, lard, and egg yolk [51].

In pharmaceutical applications, CO_2 can be used to extract drugs from sources without the chemical decomposition that results from using organic liquid solvents. Examples of extractable compounds include steroids, alkaloids, and anticancer agents.

3.3.4.6 Specialty Applications

Critical Fluid Systems, Inc. has developed a new SFE process for the recovery of oxygenated hydrocarbons from water. CO_2 is used as the solvent in a process similar to conventional

liquid-liquid extraction. The hydrocarbon is then recovered from the CO_2 by distillation and depressurization [39].

SFE is used in the polymer processing industry to remove excess monomer from polymerization reaction products, without the disadvantages found in steam stripping, e.g., high energy requirements and temperature-induced degradation [39]. Additionally, polycarbosilane polymers, which are being considered in the production of silicon carbide filaments for high-temperature applications, have also been fractionated using SCF solvents.

Supercritical CO_2 has also been used as a solvent for the application of industrial coatings as a replacement for organic solvents that emit hazardous pollutants into the air [52].

Supercritical fluids have been used to desorb contaminants from activated carbon and resinous adsorbents. A variety of organic materials were successfully desorbed from activated carbon as well as resinous adsorbents, given the appropriate extraction conditions for the particular compound [53].

Oil extraction from various media has also been demonstrated. On a semi-continuous basis, Chinese oil shales have been extracted from mined coal using toluene [54]. Supercritical toluene (716 °F and 754 psia) has been successfully demonstrated as an appropriate solvent for extraction of oil from used automotive tire samples. At the stated extraction conditions, 57% (by weight) of the original tire sample was converted to liquid oils [55].

3.3.5 Treatment System Effluent

Typically, SFE results in a concentrated product or waste stream. In the case of petroleum, food, and pharmaceutical applications, the recovered extract stream is a valuable product. In cleaning operations and hazardous waste applications, the extract stream contains a concentrated waste and must be subsequently disposed. This concentration may trigger RCRA action levels in cases where a dilute stream below the action levels is concentrated

to above the action level. In both cases, the media not extracted, including any inorganics initially present, remain unaffected by the SFE process.

3.3.6 Advantages/Disadvantages of SFE

SFE has many advantages over distillation and liquid extraction [39]. SFE processing is capable of extracting a selected compound. The solubility of a particular compound can be affected by changes in pressure, temperature, and the choice of solvent. The extract from an SFE process is virtually free of residual solvent. Nontoxic, nonhazardous supercritical CO_2 can be used without contaminating the material being processed. In SFE, the settling rate is higher for precipitates, and the mass transfer rate is improved for solvent diffusion through solid phases. The ability of the SCFs to separate nonvolatile compounds at moderate temperatures reduces the energy requirements compared to distillation.

Unlike many environmentally sensitive or toxic SFE solvents, CO_2 gas is relatively nontoxic, relatively unreactive, environmentally safe, is naturally occurring, and a metabolic byproduct of animal respiration; it therefore carries a minimal chance of occupational health risk [56]. Liquid and supercritical CO_2 is currently used in food refrigeration and processes such as the decaffeination of coffee beans [56]. Also, during the cleaning of the residues from metal parts, the evaporation of post-process CO_2 is rapid and complete when compared to typical halocarbon solvents, since CO_2 is a gas at ambient conditions. Any small amounts of sorbed CO_2 that remain after the cleaning process do not harbor the additional corrosive potential observed in halogen (i.e., derived from halocarbon) residues. Rapid evaporation of CO_2 at ambient conditions eliminates the need for significant post-cleaning "drying" times since no "solvent" residue remains. Cleaning with CO_2 is performed in a closed-loop (pressurized) system; therefore, this mode of operation essentially eliminates cleaning fluid (and its vapor) exposures to personnel and associated process equipment, which may be affected by conventional solvents. In addition, the evaporative losses to the environment are minimized because CO_2 is circulated in a closed-loop system. Using CO_2 offers a virtual 100% solvent recycle to minimize "solvent" usage rate and cost, and a sharp reduction in the process-generated waste volume.

The ROSE process offers several advantages over conventional solvent extraction processes used in the refining of petroleum crudes [40, 41, 42]. The ROSE process was developed to improve the yield and quality of products from heavy petroleum residues, using a wide variety of feedstocks and solvents. The major advantages of this process include lower utility costs and lower capital costs in comparison with conventional solvent extraction processes and reduced raw material requirements by allowing for solvent recycle and using a low-cost solvent. Also, the process can be used not only in conventional refineries, but also for field upgrading of heavy crudes, coal liquefaction, and in other areas where commercial experience in handling SCFs can be used to meet processing challenges.

While regeneration of spent activated carbon with supercritical CO_2 is possible, several limitations do exist. First is a common problem with all slurry systems, namely, the materials handling problems associated with feeding solids to a high-pressure vessel. It has also been reported that irreversibly adsorbed compounds, which are not soluble in CO_2, may build up on the carbon, precluding complete regeneration [39]. The desorption characteristics of activated carbon and resin adsorbents were studied by Arthur D. Little, Inc. Phenol was demonstrated to be nearly completely desorbed from polymeric materials as compared to the substantially less complete desorption achieved from carbonaceous and GAC materials. All adsorbents had been initially saturated with a 2,200-mg/L phenol solution [53]. Nearly complete desorption of the pesticide Aloclor was demonstrated for activated carbon and a polymeric resin using carbon dioxide as a solvent [53].

There are several potential disadvantages to SFE processing. First, the capital and energy costs may be higher than those associated with other technologies. Energy costs are largely due to the repeated heating and compression of the solvent. Capital costs are driven by the requirement to withstand the high pressures used during operation. These high pressures also indicate that safety issues must be carefully considered. The advantages and disadvantages associated with SFE technology are highly application-specific and must be evaluated on a case-by-case basis.

3.4 EXPERT CONTACTS AND VISITS

In order to obtain the most current information in the application of supercritical fluid technologies, a number of experts were contacted. Telephone interviews and site visits were conducted. Table 3-4 is a list of the technical experts contacted and interviewed and highlights of their current work. The information gained during these interviews has been incorporated into the literature reviews and technology evaluations as appropriate. Brief discussions of these interviews are presented in this subsection.

A site visit and meeting with Dr. Robert Alhert of Rutgers University, Rutgers, NJ, offered an opportunity to inspect a 20 cm^3 bench-scale SFE system. Current work in the unit is focused on extraction of PCB from contaminated soils using supercritical CO_2. Previous work has included measurement of solubilities of fine PAHs as a function of temperature and pressure leading to the development of a thermodynamic model as well as measurement of PAH adsorption equilibria and modeling of PAH desorption from soil. The results of this research are described in Subsection 3.3. Dr. Alhert stated that SFE will be limited by process economics to situations where the manufacturing end product is expensive, high temperatures and pressures are required, or extremely dangerous or hazardous goods are involved [9].

Carl Janson of Riordan Materials Corporation conducted a tour of an operating Zimpro wet-air oxidation (WAO) unit at the Mt. Holly, NJ, Wastewater Treatment Plant. This unit is being successfully used for powdered activated carbon regeneration. As is common with WAO applications, complete organic oxidation of contaminants does not occur. This process does, however, operate similarly to a SCWO unit in that slurried waste is blended with an oxidant source, preheated, and injected into a reactor where oxidation occurs. Because of the system similarities to SCWO, the WAO unit was investigated even though it is a subcritical process. Because of the relatively mild conditions used in WAO [480 °C (896 °F) and 6.2 MPa (900 psia)], the reaction time is significantly greater than that needed for SCWO. As such, the reactor has a considerably larger volume in a WAO process than for a corresponding throughput in a SCWO system.

Table 3-4

Expert Contacts and Site Visits Summary

Contact	Interview Method	Technology Highlights
Dr. Robert Albert Rutgers University Piscataway, NJ	Telephone conversation and site visit.	• Bench-scale SFE unit operating. • SFE applicable for: (1) manufacturing processes with expensive end product; (2) applications requiring high temperature and high pressure; and (3) processing involving extremely dangerous or hazardous goods.
Carl Janson Riordan Materials Corporation Blue Bell, PA	Telephone conversation and site visit to operating Zimpro Unit at Mt. Holly, NJ, wastewater treatment plant.	• Zimpro is a WAO (sub-critical) process. Because of large scale, and similarity to SCF processes, site was visited. • Used for carbon regeneration application. • Complete organic oxidation is not obtained with WAO processes.
Susan Erickson CF Systems Woburn, MA	Telephone conversation and site visit.	• CFS has full-scale extraction experience. • Currently focusing on extraction of organics with propane at ambient temperatures and elevated pressures. • Mobile and transportable units available. • Ongoing work in attempting to add chemical agents to effect metals precipitation. Currently metals remain unaffected during process.
Dr. Jefferson Tester Dr. William Peters Massachusetts Institute of Technology - Energy Laboratory Boston, MA	Telephone conversation and site visit with Dr. Peters.	• Studying theoretical aspects of SCWO: - Applied Process Engineering and Simulation. - Engineering Science. - Molecular Modeling of Phase Reaction Kinetics and Separations.
Ramin Abrishmian Remediation Technologies, Inc. Concord, MA	Telephone conversation.	• Has done past work on SFE for USAEC. • Worked with CFS. • No current work in area of SFE.
John Moses CF Technologies, Inc. Hyde Park, MA	Telephone conversation.	• Most of CF Technologies work is proprietary and/or under government contract. Only limited information is available to the public. • Pilot-scale unit is under construction.

Table 3-4

Expert Contacts and Site Visits Summary
(Continued)

Contact	Interview Method	Technology Highlights
Michael Spritzer Daniel Jensen General Atomics San Diego, CA	Telephone conversation.	• Working in SCWO. • Teamed with EcoWaste Technologies and the University of Texas at Austin. • Small pilot plant for treating 100 mL/min of triple-based propellant. • Two laboratory-scale lined SCWO reactors for corrosion testing. • Contract focusing on treatment of warfare agents, propellants, and highly chlorinated compounds. • Munitions disposal research and development since 1982. • 1500 gpd skid-mounted unit for chemical weapons destruction under construction. • Soil treatment could present a materials handling problem in terms of plugging in valves. • General Atomics considers scale-up and reliability as major issues. • Transportable units available.

Table 3-4

Expert Contacts and Site Visits Summary
(Continued)

Contact	Interview Method	Technology Highlights

Dr. Earnest Gloyna
Dr. Lioxing Li
University of Texas at Austin
Balcones Research Center
Austin, TX
	Telephone conversation and site visit.	● Involved in SCWO.
		● Bench- and pilot-scale (40 gph) operating units.
		● Predominantly have tested aqueous solutions, but have done pumping tests on slurried soils.
		● Corrosion studies ongoing.
		● Range of wastes tested:
		  - Insecticides
		  - Pesticides
		  - Herbicides
		  - EPA priority pollutants
		  - Chemical warfare agents
		  - Propellants
		  - Domestic waste
		  - Biological waste

Richard Lyon EcoWaste Technologies Austin, TX	Telephone conversation and site visit.	● Commercial SCWO unit for Texaco. ● Teamed with General Atomics on DARPA and Air Force projects.
Jack Davis Kem-Shredder Corporation Austin, TX	Telephone conversation and site visit.	● Hydrogen peroxide as oxidant. ● Mobile 1/2 gpm unit available. ● Could provide mobile unit up to 2 gpm size.
Glen Hong Modar, Inc. Natick, MA	Telephone conversation and site visit.	● 500-gpd pilot plant on-site. ● Bench-scale unit on-site. ● Bench-scale work performed on DNT. ● Inorganic salt formations in reactor are a drawback.
Dr. Richard Oldenborg Los Alamos Laboratories Los Alamos, NM	Telephone conversation.	● SCF technologies being applied to nitrate salts in simulated Hanford tank waste. ● SCWO work being done on triple-based propellant.
Ed Modell Modec Framingham, MA	Telephone conversation.	● Pilot-scale unit next year. ● SCWO processing of sewage sludge in pilot unit.

Table 3-4

Expert Contacts and Site Visits Summary
(Continued)

Contact	Interview Method	Technology Highlights
Dr. Lalith Kumar Thar Designs, Inc. Pittsburgh, PA	Telephone conversation.	• Research and manufacturing of SFE and SCWO equipment. • Confidential materials research ongoing.
D. Larry Taylor Virginia Polytechnic Institute and State University (VPI) Blacksburg, VA	Telephone conversation.	• Nitroglycerine (NG) extraction from single- and double-based propellants with 90% demonstrated efficiency. • Diluent added to extract stream.
Dr. Robert Farncomb Naval Surface Warfare Center (NSWC) Indian Head, MD	Telephone conversation.	• Based on Dr. Taylor's bench-scale work. • DNT and NG extractions. • 500 mL vessel using 25 g of propellant.
Robert Shaw Army Research Office (ARO) Research Triangle Park, NC	Telephone conversation.	• Funding fundamental SCWO research.

CFS has demonstrated full-scale extraction experience. Although much of its demonstration work [10] has been with supercritical CO_2 extraction, recently CFS has focused on extraction with propane at ambient temperature. Therefore, portions of its current research are not appropriate for evaluation as a supercritical fluid technology. As in the case of WAO, however, information gained from this similar subcritical fluid process is applicable to supercritical fluid extraction because of process similarities. Results of CFS SFE studies are reported in Subsection 3.3.

Work at the MIT Energy Laboratory has focused on theoretical aspects of SCWO processing. Research and simulation have focused on Reactor Engineering and Process Simulation Modeling. Work in the area of Engineering Science has included Engineering Kinetics of Waste Destruction, Corrosion of Construction Materials, and Nucleation and Phase Separation Kinetics. Research has also been conducted in Molecular Modeling of Reaction Kinetics of Phase Separations.

Ramin Abrishmian of Remediation Technologies, Inc. was contacted for a telephone interview as he has previously worked in the area of supercritical fluid technology. Although he is not currently pursuing SCF research, he supplied additional contacts performing current work.

General Atomics has teamed with EcoWaste Technology and the University of Texas at Austin. They have completed a small pilot-plant for treating 100 mL/min of propellants and are currently constructing a 1,500 gpd skid-mounted pilot plant for chemical weapons destruction. Other current capabilities include two laboratory-scale lined SCWO reactors used in corrosion testing, on-going munitions research and development efforts, and availability of pilot-scale units for purchase. General Atomics is currently under contract focusing on warfare agents, propellants, and highly chlorinated compounds. General Atomics has focused its work to date on aqueous systems, but considers soil processing to be technically feasible. General Atomics cautions, however, that additional work will be needed to resolve the materials handling problems associated with pumping a non-homogeneous mixture through a series of valves without clogging. Future scale-up from the

current pilot-scale size and process reliability are additional challenges facing future operations. Technical feasibility and economic informatio: supplied by General Atomics has been incorporated into Section 4.

It should be noted that General Atomics does not make an effort to separate salts during processing. Its approach is to maintain a sufficient fluid velocity to entrain any solids throughout the reactor length. In the case of solids that adhere to reactor surfaces during processing, General Atomics' approach is to operate two identical reactors in parallel. One reactor at a time is in use. When solids build up such that heat transfer is affected or clogging may occur, flow is switched to the other reactor. The fouled reactor would then be rinsed with water at ambient conditions. Since the salts which were insoluble in supercritical water are soluble in water at ambient conditions, the salts are redissolved and reactor is left clean.

The University of Texas at Austin has been conducting research in SCWO since 1989. Both bench- and pilot-scale units are currently available. A wide variety of materials (listed in Table 3-1) have been tested. Additionally, soil slurries have been successfully tested for pumpability. Reactor material corrosion is viewed as a major issue for future development and much of the current research effort is focused in this area. Information concerning SCWO research at the University of Texas at Austin is found in Subsection 3.2.

Another technology vendor associated with the General Atomics and University of Texas team is EcoWaste Technologies (EWT). EWT currently is constructing a pilot-scale commercial unit for Texaco in the Austin area to process petrochemical wastes. They have teamed with General Atomics on various government research projects, as well as the construction of the current pilot-scale unit for chemical warfare agent destruction.

A newly-formed corporation, Kem-Shredder Corporation, located in Austin, Texas, is performing SCWO with hydrogen peroxide as the oxidant source. Currently, Kem-Shredder has a 0.5 gpm mobile unit available for treatment of aqueous feed. They feel that the

mobile unit is ready to be scaled up to a 2-gpm capacity. With modifications for materials handling considerations, this unit could be used for treatment of slurried soils.

Modar, Inc. currently operates a 500-gpd SCWO unit as well as a bench-scale unit on-site. Bench- and pilot-scale work has been conducted on a variety of wastes, including bench-scale testing of DNT destruction. They claim to have treated solvent wastes including PCE and TCE. Modar typically monitors vapor emissions from the reactor for air compliance parameters. Modar does not recommend treatment of electroplating waste by SCWO because of the waste's low heating value, corresponding to its low organic content, which would make it difficult to sustain oxidation. The biggest processing difficulty noted by Modar is the formation of inorganic salts during treatment. Some salt precipitates are easily separated under supercritical conditions. Other salts, including many sodium compounds, tend to adhere to the reactor wall and make separation difficult. Technical feasibility and economic information supplied by Modar is considered in Section 4.

Dr. Richard Oldenborg was contacted regarding current research at Los Alamos Laboratories. Dr. Oldenborg described the nitrate reduction work which is being conducted on simulated Hanford tank wastes, as discussed in Subsection 3.2. Los Alamos is also conducting research in SCWO of triple-based propellants. Destruction of greater than 99.9% has been demonstrated. This research is also discussed in Subsection 3.2.

Dr. Larry Taylor of VPI and Dr. Robert Farncomb of NSWC are also conducting research on the area of explosives extraction. Dr. Taylor's research has been conducted on the bench-scale with propellant quantities no greater than 1 gram being used. Extraction of NG from single- and double-based propellants using supercritical CO_2 has been accomplished with a demonstrated efficiency of approximately 90%. This research has been scaled up by Dr. Robert Farncomb. Dr. Farncomb has performed extractions on 25 g of propellant in a 500 mL reactor. Dinitrotoluene (DNT) and NG have been extracted from single- and double-based propellants. Dr. Farncomb plans to begin extractions with a 2.5 L extraction unit in the near future. Both Dr. Taylor and Dr. Farncomb add diluents to the CO_2/explosive stream prior to pressure release to separate the CO_2. The diluent is added

such that the explosive stream after CO_2 removal contains no more than 40% explosives. Neither researcher has reported any detonations in the extract stream. Potential applicability of this research as well as Dr. Oldenborg's findings will be discussed more fully in Section 4.

Dr. Lalith Kumar of Thar Designs, Inc. conducts research and manufactures SFE and SCWO processing equipment. Much of his current work is proprietary and confidential and thus cannot be divulged in this report. However, it can be stated that research is focusing on development of cost-effective, reliable processing equipment with special emphasis being placed on materials of construction. Pilot-scale SFE units are available. A pilot-scale SCWO unit should be available soon.

Ed Modell of Modell Development Corporation (Modec) stated that it currently has a 500-gpd SCWO pilot plant under construction. The unit will be skid-mounted and transportable. It will be available in 4 or 5 modules and will have approximate dimensions of 200 ft long by 30 ft wide. Modec has performed bench-scale SCWO testing on 2 varieties of aqueous and sludge wastes. Pilot-plant trial runs will be performed on sewage sludge.

Robert Shaw of the Army Research Office (ARO) is funding fundamental research pertaining to SCWO processing. Specific areas of research include addressing corrosion problems, salt precipitation, and reactor design. ARO is primarily interested in the treatment of chemical weapons agents and explosives and propellants.

Finally, a rocket motor demilitarization demonstration project is being conducted for the U.S. Air Force at Armstrong Laboratory. Details of this work were not available for inclusion in this report.

3.5 TECHNOLOGY STATUS

Currently, SFE and SCWO technologies are available at both bench- and pilot-scale. One full-scale SFE unit is currently in operation.

Table 3-5 is a summary of the current SCF technology status. Pilot-scale SCWO units are available from General Atomics, Modar, and EcoWaste Technologies. A pilot unit is also available for testing at the University of Texas at Austin. Additionally, a small mobile unit is available (0.5 gpm with potential to 2 gpm) from Kem-Shredder Corporation. All the vendors discussed are capable of performing bench-scale experiments to determine appropriate kinetic parameters and on-site pilot units to perform trial runs for specific wastes prior to constructing a pilot-scale reactor. Kem-Shredder Corporation's unit is trailer mounted and could easily be transported to a site. The remaining units would be considered to be transportable and are available as skid-mounted units. The University of Texas at Austin has been included in this section because it has a functional pilot-scale unit on-site. As has been discussed, a variety of wastes have been tested in this facility. This pilot unit could be a convenient site for initial testing of an undemonstrated waste type.

Fewer vendors are commercially pursuing the area of supercritical fluid extraction. Although CFS has a full-scale operating unit and the capability for bench- and pilot-scale testing, their current interests are in extraction with ambient temperature propane because of a reported cost advantage [10]. CF Technologies currently has a bench-scale supercritical extraction unit. Additionally, it is constructing a pilot-scale unit which should be available in the near future. As in the case of the SCWO unit, the University of Texas at Austin also has a pilot-scale SFE unit. Again, the potential exists for initial testing to be conducted at the University.

Table 3-5

Technology Status Summary

Vendor	Technology	Available Units
General Atomics	SCWO	bench-scale; pilot-scale
Modar, Inc.	SCWO	bench-scale; pilot-scale
EcoWaste Technologies	SCWO	bench-scale; pilot-scale
Kem-Shredder Corporation	SCWO	mobile unit
Modec	SCWO	pilot-scale unit under construction
University of Texas @ Austin	SCWO	bench-scale; pilot-scale
CF System	SFE	bench-scale; pilot-scale; full-scale
CF Technologies	SFE	bench-scale
University of Texas @ Austin	SFE	bench-scale; pilot-scale
Thar Design	SFE	pilot-scale

SECTION 4

TECHNICAL EVALUATION

4.1 TECHNICAL EVALUATION CRITERIA

The following criteria were used to evaluate SCF technologies:

- Capability of removing and destroying hazardous waste components to concentrations defined in applicable laws and standards.

- Ability to remove or destroy surface contamination without complete destruction of the carrier material.

- Nonspecificity in treating varieties of hazardous waste materials.

- Identification of waste residues generated.

- Potential safety hazards associated with treating explosives-contaminated materials.

- Capability of treatment at the source or site of the contamination within the schedule of an Installation Restoration (IR) Program.

- Permittability and public acceptability.

- Operational reliability and demonstrated performance and safety data.

- Cost-effectiveness in comparison to alternative treatment methods.

- Consideration of system materials of construction.

4.1.1 Capability of Removing and Destroying Hazardous Waste Components

To evaluate the applicability of SCF technologies to the waste scenarios described in Section 2, the ability of each respective technology to remove the specified contaminants from the required media will be discussed including demonstrated treatment efficiencies where possible. As part of the evaluation of SCF technology effectiveness, it is desirable to determine the ability of each treatment technology to reduce the contaminant concentration in each waste scenario to levels that may be specified under applicable laws and standards. Because laws and standards are largely determined by regional and state regulations as well

as various site-specific factors, it is not possible to formulate a single set of treatment criteria that would be broadly applicable to the waste scenarios described in Section 2. The capability to treat the specified components will be evaluated on the basis of available treatment efficiencies and probable results for undemonstrated components based on performance with similar constituents.

4.1.2 Ability to Remove or Destroy Surface Contamination Without Complete Destruction of the Carrier Material

SCF technologies will be evaluated based on their ability to remove contamination from contaminated material (such as equipment or contaminated environmental media) without complete destruction of the carrier material or medium. Potential carrier materials include items such as wood, shell casings, or machinery parts. The ability to remove contamination from such items without destroying essential properties of the item is critical to the use of SCFs as a decontamination technology. This evaluation will first consider the effect of the SCF technology unit operation on the carrier material. Second, the effect of any necessary materials-handling steps on the carrier material will be discussed. For example, in order to treat a solid material in a continuous flow system, the material must be reduced in size and slurried or solubilized so that a pumpable solution is formed.

4.1.3 Nonspecifity in Treating Varieties of Hazardous Waste Materials

Since the waste scenarios described in Section 2 contain more than one component, the ability of each SCF technology to destroy or remove all contaminants present or to destroy or remove one targeted component from the mixture will be evaluated. In the waste scenarios described in Section 2, it will most often be preferable to destroy all waste components. Techniques will be evaluated on their ability to treat organic and inorganic wastes. Additionally, removal or destruction of only portions of a category of waste (for example, the ability to extract the organic material from a mixture of several components) will be considere'.

4.1.4 Identification of Waste Residues Generated

Potential waste streams generated during SCF processing will be evaluated. These streams may include air emissions, liquid effluent, any solid residues, feed material unaffected by treatment, as well as excess solvents and modifiers. The waste streams from any given process will be determined by the process type (SFE or SCWO), contaminants present, treatment efficiency, and media type. Potential residues from treatment of each waste scenario by SFE and SCWO will be discussed.

4.1.5 Potential Safety Hazards Associated With Treating Explosives-Contaminated Materials

For both SFE and SCWO technologies, potential safety hazards associated with the treatment of energetic materials will be discussed. Safety hazards may occur during materials-handling steps prior to treatment, during the treatment process itself, and in handling of any streams generated during the process which contain explosive materials. In the case of the three waste scenarios that involve explosive materials, specific materials-handling requirements and limitations will be discussed as they apply to SFE and SCWO processing.

4.1.6 Capability of Treatment at the Source or Site of the Contamination Within the Schedule of an Installation Restoration (IR) Program

Evaluation of the capability of a given SCF technology to treat at the source or site of the contamination within potential schedules that may be applied under the IR Program involves discussion of two distinct criteria. First, the ability to adequately develop technology for implementation in the near future (i.e., within 5 years) will be discussed. Second, in order to determine the ability to cost-effectively treat contaminated materials on-site, the potential availability of mobile or transportable SCF units to complete treatment within the potential schedule of an IR Program will be discussed. Just as there are no universally applicable remedial cleanup criteria, there is no universally applicable cleanup schedule. For purposes of this evaluation, realistic remedial cleanup periods, based on available information, will

be used. This ability will be determined by the potential capacity of the processing equipment as well as the remediation schedule established for an individual project.

4.1.7 Permittability and Public Acceptability

The evaluation of potential permittability and public acceptability issues will be based largely on professional judgment and experience, as expressed in literature and through personal communication with SCF experts. Applicable federal laws and regulations with respect to environmental discharge permits can serve as overall guidelines. However, specific permitting requirements may vary depending upon specific site location in terms of EPA regions, state and local programs. It should be recognized that, under most regulatory programs, state agencies can receive permission to administer environmental programs only when state programs are at least as stringent as federal requirements. Consequently, state requirements may exceed those specified in federal laws and regulations.

4.1.8 Operational Reliability and Demonstrated Performance and Safety Data

Because of the limited number of pilot- and full-scale SCF technology units that are currently in operation, information regarding operational reliability and demonstrated performance and safety data is limited. Evaluation in this area will be based on existing data as well as professional judgment based on performance to date.

4.1.9 Cost-Effectiveness in Comparison to Alternative Methods

The cost-effectiveness of SFE and SCWO technologies in comparison to alternative treatment methods will be evaluated. Only those scenarios that are deemed to be technically feasible based on the other evaluation criteria will be evaluated. Available cost information on SCF technologies is limited, as only a small number of pilot scale units have been constructed and operated. However, the data that are available for capital and operating and maintenance (O&M) costs will be incorporated with the costs associated with auxiliary materials-handling equipment (where needed) to estimate overall project costs.

Capital, annual O&M costs, and present worth costs for the projected project life will be presented. Additionally, the cost per unit of material to be treated over the projected project life will be estimated.

4.1.10 Consideration of System Materials of Construction

Finally, consideration will be given to the system materials of construction. The materials used for unit fabrication strongly affect the SCF unit capital cost. Additionally, as discussed in Section 3, system reliability and anticipated useful life are dependent on the corrosion-resistance of the materials chosen.

4.2 EVALUATION OF TECHNOLOGIES

The technical feasibility of applying supercritical fluid techniques to the waste scenarios is evaluated in this section. This evaluation will be based on the criteria described in Subsection 4.1.

4.2.1 Capability of Removing and Destroying Hazardous Waste Components

As discussed in Section 3, both SFE and SCWO are capable of treating organic contaminants to high removal or destruction efficiencies. In the case of SFE, the contaminants are concentrated in an extract stream and are then available for recycle, disposal, or subsequent destruction by other means. SCWO offers the potential for direct destruction of organic contaminants. Due to a lack of specific treatment performance data for the targeted waste scenario and uncertainty as to the applicable treatment levels, firm conclusions concerning the ability of each technology to treat those wastes to regulatory levels cannot be drawn.

The waste scenarios described in Section 2 contain several explosive materials. Explosives are components of the OB/OD, lagoon sediment, and repacking plant wastewater scenarios. SFE processing of explosives-containing materials result in the production of an

extract stream containing a high concentration of explosives. Although extraction and concentration could allow for material recycle, the safety hazards associated with a concentrated explosive stream are prohibitive. Recent studies at Los Alamos National Laboratories involving extraction of nitroglycerin from a triple-based propellant resulted in "popping" in the extract stream, presumably from small detonations [4]. Since this work was being conducted at the bench-scale, the extent of the reactivity hazard at larger scales is uncertain.

Work has been recently conducted involving extraction of energetic materials from propellant systems. In particular, dinitrotoluene (DNT) has been extracted from a single-based propellant and nitroglycerin has been extracted from a double-based propellant [57]. In both cases, a 500 ml vessel was used with 25 grams of propellant being initially loaded into the extraction vessel. Supercritical CO_2 was used as the extraction fluid. To avoid the potential safety hazards associated with handling a concentrated explosive stream, a diluent was added to the CO_2/explosive stream prior to pressure reduction [57]. Similar work at a smaller scale has also been conducted. In this bench-scale work, nitroglycerin has been extracted from single- and double-based propellants with extraction efficiencies of approximately 90% being achieved [58]. A diluent was also used in this case in the extract stream to avoid potential safety hazards. The bench-scale tests have been conducted with initial quantities of less than 1 gram of propellant [58]. Although these results show promise in alleviating the safety ha.... associated with extracting explosives, it must be noted that these are still laboratory-s.... operations and not fully engineered systems. In fact, much of the bench-scale work done to date has focused on use in analytical techniques. Also, although this extraction procedure could separate an explosive material from a propellant mixture, the resulting diluent/explosive mixture would have to be subsequently managed. The volume and characteristics of the final, diluted waste would determine how it would be managed. This technique has not been demonstrated for explosive-contaminated soils.

Explosives treatment by SCWO has been demonstrated only at the bench-scale. Recently, a demonstration of 2,4-dinitrotoluene (DNT) in aqueous solution destruction by SCWO was conducted [17]. This study showed a >99% reduction in total organic carbon (TOC) (used

as a surrogate for specific DNT analyses) with SCWO treatment. The reaction conditions reported were 528°C (982°F), 29 MPa (4,200 psi), and a 3-minute residence time. Additionally, DNT process wastewater has been treated by SCWO. In this case, 99.6% removal of total organic carbon (TOC) was achieved in 7 minutes [350°C (662°F) and 27.6 MPa (4,000 psi)] [33]. Subcritical wet air oxidation [320°C (608°F), 1.3 MPa (190 psi), 1 hour residence time] has been demonstrated as a feasible technology for 2,4,6-trinitroluene (TNT) simulated wastewater but the long residence time is prohibitive. Greater than a 95% reduction in TOC was achieved in a batch run[4]. In all of these tests, dilute streams were used for safety precautions. Propellant destruction has also been demonstrated at the University of Texas at Austin[8]. Destruction efficiencies and reaction conditions for these runs are not available. Communications with various sources from universities and industry [8, 14, 59, 60] indicate that explosive destruction by SCWO is ready for pilot-scale demonstration. Explosives destruction projects have not been widely conducted due to a lack of industrial interest [14] and not having the necessary permits to use explosive materials [60].

Chlorinated hydrocarbons have reportedly been successfully extracted from soils and aqueous solutions using SFE technology [9, 12]. Work has focused primarily on removal of polychlorinated biphenyls (PCBs) from soils. PCB extraction from soil has been reported to be >90% efficient [61] with efficiencies reported up to 99.7% [45]. After concentrating the PCBs in the extract stream, an additional destruction step such as SCWO or incineration would be required.

Although concentration of other chlorinated hydrocarbons, including common solvents, by SFE would likely be technically feasible, it may not be economically attractive. If SFE techniques were used and recycle was not desirable, a subsequent destruction step would be needed. Also, depending on the exact components present, separation of only one component from a mixture for purposes of recycling may not be possible. This process would not offer any readily apparent advantages over conventional techniques for removal and/or destruction of solvents.

Destruction of various chlorinated hydrocarbons by SCWO has been demonstrated. The major barrier to implementation of SCWO for chlorinated hydrocarbon treatment is in controlling corrosion in the SCWO process equipment. In order to limit corrosion, the feedstock and/or acids formed during oxidation must be neutralized for pH adjustment purposes prior to entering the reactor. This neutralization has commonly been accomplished through addition of agents such as NaOH or $Ca(OH)_2$ [23]. The resulting sodium or calcium salts (NaCl and Na_2SO_4 or $CaCl_2$, and $CaSO_4$) are prone to depositing on the reactor and are insoluble at supercritical conditions and lead to system plugging. As discussed in Section 3, solids separation techniques are being developed in an effort to control such problems [8, 60].

Paint wastes containing both organic and inorganic fractions are another potential stream for treatment by SCF technologies. As discussed in Section 2, the wastes from painting operations contain approximately equal organic and inorganic fractions. The organic fraction of painting and paint stripping operations consists of paint strippers and solvents as well as the paints' polyurethane or epoxy base. The inorganic fraction contains metals such as chromium, iron, nickel, and titanium.

SFE would likely be capable of removing the organic constituents of paint and paint wastes. Although no data were found indicating that epoxies and polyurethanes could be extracted using supercritical fluids, because of the wide variety of organic compounds that are soluble in supercritical fluids, it seems likely that an appropriate fluid and operating condition could be found to make this extraction viable. Testing would be required to verify process viability. The organic components would be concentrated in the extract and would require subsequent destruction or disposal. Since the recycle value of these constituents is uncertain, advantages would depend on the solvent recycle value. The inorganic constituents would remain unchanged by the SFE process and would be present in the system effluent or precipitate.

SCWO techniques may also be applicable to the destruction of the organic fraction of paint waste. However, no specific data were found for epoxies or polyurethanes. The inorganic

paint fractions that are water-soluble at ambient conditions will be insoluble in supercritical water and will precipitate. A solids removal step within supercritical conditions will, therefore, be required. New solids separation techniques, discussed in Section 3, have been developed that will aid in solids handling [8, 60]. These techniques involve either mechanical separation while in the supercritical state or a system such as the Modar three-phase reactor, which automatically separates the solids by gravity [23].

Based upon information presented in Section 2, electroplating wastes consist primarily of inorganic materials. As such, SFE would be largely ineffective in treating electroplating wastes. It may be possible to precipitate out metals in the supercritical state through chemical addition if a high value or highly toxic metal is present.

SCWO may be applicable to the destruction of cyanide and organic cyanide complexes. However, SCWO would not be applicable to treatment of electroplating waste streams. Although the metals found in the electroplating stream would precipitate out in supercritical conditions, there are a variety of other conventional techniques available to accomplish this separation. Additionally, as described in Section 3, trivalent chromium is oxidized to hexavalent chromium under SCWO conditions.

4.2.2 Ability to Remove or Destroy Surface Contamination Without Complete Destruction of the Carrier Material

When evaluating the ability of SFE and SCWO technologies to remove or destroy contamination without complete destruction of the carrier material, several factors must be considered. First, the types of carrier materials involved in the specified waste scenarios are important. In the waste scenarios, one type of material is contaminated soil or sediment. Additionally, other materials, such as contaminated wood, machinery, tools, and personal protective equipment, may be present at Army Installations as a result of either industrial operations or as part of remedial action activities. Second, the effect of the SFE or SCWO unit process itself on the carrier material must be considered. In conjunction with this, any required materials-handling steps that must be performed before or after the SCF unit process that may affect the carrier material must be considered.

In pilot- or full-scale operations, SFE may be operated in a batch or continuous mode. Soils and other solid media are amenable to batch processing with SFE techniques. The media would be loaded into the batch reactor and the supercritical fluid circulated through the media to effect the extraction. The media that was not extracted would remain unaffected by the process.

In the case of soil extraction, SFE removes organic contaminants from the soil, leaving the matrix largely unaffected [9,10]. If CO_2 is used as the extracting fluid, the fluid is returned to the gas phase at ambient conditions, leaving no residue in the soil [9]. This technique would be potentially applicable to soils contaminated with chlorinated hydrocarbons and petroleum products. Also, if safety considerations are sufficiently resolved, this technique could be used to extract explosive material from contaminated soils and sediments. Finally, although not part of the specified waste scenarios, SFE is capable of extracting surface contamination from materials such as tools or machinery parts. Economic considerations may limit the parts that can be treated because of size constraints.

To be economically effective, it may be necessary in some circumstances to run SCWO processes on a continuous basis [8]. This is due to the high energy costs associated with pressurizing and depressurizing the system. Only materials that are pumpable or can be slurried to become pumpable can be continuously treated by SCWO. In the case of explosives-contaminated soils and sediments, the solids must be slurried prior to pumping. This would involve a materials separation scheme to remove large rocks and debris from the soil followed by a blending step with water to form a slurry. In the case of propellants, the material may have to be reduced in size or hydrolyzed to become water soluble prior to slurrying with water. Although pumps capable of transporting slurried soil exist, the specific concentration at which a given soil is pumpable must be determined on a case-by-case basis. Additionally, the particles must be small enough and at a sufficiently low concentration such that clogging does not occur in the system valves. Development of soils specifically designed for use with soils could allow a higher concentration of soils to be processed. The specific particle size that is pumpable will depend on particle morphology and system configuration. In all cases, special care must be used in handling due to the

reactive nature of the material. Batch SCWO processing of materials may be possible, but has only been accomplished at the bench-scale.

4.2.3 Nonspecificity in Treating Varieties of Hazardous Waste Materials

In the case of SCWO processing, organic contaminants are completely destroyed, given the proper set of operating conditions. No literature data were found that would indicate that selectivity within organic compounds would be possible. It seems unlikely that the reaction parameters could be controlled such that only selective organics are destroyed while other organics are not oxidized. This complete organic destruction would be advantageous in cases where a variety of organic materials are to be treated, and selectivity is not desired.

Depending on the treatment method chosen, SCF technologies may be capable of targeting only specific constituents within a mixture. Since SFE depends on the solubility of the individual organic contaminant in the solvent at a set of specific supercritical conditions to effect extraction, by varying the extraction fluid and/or processing conditions, specific contaminants may be targeted. Therefore, SFE can be considered capable of extracting specific organic contaminants in some cases. This property is potentially useful for the paint waste scenario in which it may be possible to extract a specific solvent from the mixed waste. The feasibility of this would depend on the constituent's individual solubilities in a given fluid and operating condition. Development and testing would be required prior to implementation.

SFE selectivity has also been demonstrated in the area of explosive materials during the extraction of one energetic material from a multi-component propellant [13, 57, 58].

4.2.4 Identification of Waste Residues Generated

Waste residues would be generated during SFE and SCWO processing. SFE treatment produces a concentrated liquid extract stream. The supercritical fluid is separated from the targeted extract, often by a simple pressure reduction step, and the extraction fluid is

recompressed and recycled to the extraction vessel. Depending on the contents of the extract stream, it may have value as a recyclable material or could be subsequently destroyed or disposed. SFE leaves the original solid or liquid media intact, except for removing the extractable component. In the case of the paint waste scenario, this remaining sludge would require disposal. Depending upon their constituents and properties, these residuals may still be regulated hazardous wastes or have hazardous properties. In some cases, concentration may trigger RCRA action levels. For contaminated soils, once the extraction is complete, the soils could potentially be returned to the excavation site for disposition, depending on regulatory considerations.

SCWO processing generates three distinct waste streams: an air emission, a liquid effluent, and a solid residue. As discussed in Section 3.2, organic carbon and nitrogen compounds are oxidized primarily to CO_2, H_2O, and N_2 (with small amounts of N_2O present) under proper oxidative conditions. If incomplete oxidation occurs due to system upset, other materials may also be present in the gaseous effluent. The liquid effluent consists largely of the reaction medium. The water commonly contains chloride ions up to their solubility limits from any chlorine-containing materials, sulfates from sulfur, and phosphates from phosphorus. Other compounds may also be present, depending on the influent constituents. Finally, metals and certain other inorganics, when present in the influent, will form salts in the supercritical environment. These salts could potentially be separated from the liquid in the supercritical environment. If they are not separated, they will be present in the liquid effluent. In the case of the specified waste scenarios, chlorinated hydrocarbons would likely be oxidized to CO_2 and H_2O with the chloride ions remaining in solution. Polyurethane and epoxy materials may also be oxidized. The exact nature of the resulting residues is not known. Likewise, the products resulting from explosive material oxidation are not known. While the degradation products of these chemical compounds (urethanes, epoxies, and explosives) may be predictable based upon chemical structure, specific products formulated from these chemicals may contain other additives or agents depending upon their use. The nature of such additives or agents need to be considered in determining products for specific SFC/SCWO applications.

4.2.5 Potential Safety Hazards Associated with Treating Explosives-Contaminated Materials

As discussed in Subsection 4.2.1, there are potential safety hazards associated with the handling and processing of energetic materials. SFE processing of explosives-containing materials will result in the production of a concentrated explosives stream. As previously stated, small detonations have been noted in bench-scale extraction of nitroglycerin from propellant. However, preliminary information indicates that the use of a diluent introduced into the extract stream prior to the pressure reduction step to remove the solvent has enabled nitroglycerin and DNT extraction without detonations [57, 58]. Determination of proper safety precautions would be imperative prior to implementation of a pilot-scale extraction process for explosives removal.

Since SCWO processing is intended to destroy organic materials, a concentrated explosive stream will not likely be generated in a properly operated system. The primary safety concern for SCWO processing of explosive materials would then be in the materials-handling steps prior to treatment. The explosive material in the OB/OD waste scenario would likely undergo a size reduction step and be hydrolyzed and solubilized in water prior to SCWO treatment. Appropriate safety precautions would need to be identified for each of these materials-handling steps prior to a pilot-scale demonstration.

4.2.6 Capability of Treatment at the Source or Site of the Contamination Within the Schedule of an Installation Restoration (IR) Program

The capability of an SCF technology to treat contaminated materials at the source or site of the contamination may be evaluated based on the availability of mobile or transportable treatment units. For waste treatment at the source of manufacture, mobility would not be an issue of concern. As stated in Section 3, both SFE and SCWO transportable units are available. Additionally, a small mobile SCWO unit is commercially available. Information regarding the suppliers of these units is presented in Section 3.

Evaluation of the capability of the available units to treat the contaminated material within the schedule of an IR Program is dependent on the schedule established for an individual site. Based upon kinetic information presented in Subsection 3.2, SCF systems offer the potential for relatively rapid treatment and, therefore, high throughput for a given reactor volume. This suggests that SCF technologies offer a high potential for treatment of wastes within potential remedial action schedule requirements, assuming successful scaleup from existing small laboratory-scale test systems. As with other reactor-based remedial technologies, increasing throughput to meet remedial schedule requirements could be accomplished (for a given set of process conditions) by increasing the scale of the reactor or by using multiple reactors. The former possibility may be limited by process-specific scaleup constraints, while the latter option would most likely be limited by economical constraints. In Subsection 4.2.9, unit sizes required to treat the specified waste scenarios will be discussed. Again, the adequacy of these capacities will be determined on an individual basis dependent on specific IR schedules. An additional factor to be considered in evaluating the potential for SCF technologies to meet IR Program schedules is the near-term technology maturity. SFE and SCWO units are currently available for pilot-scale operations, but they are still being manufactured individually and thus a substantial lead time is involved. Also, there are still many technology issues that need to be addressed for individual cases.

4.2.7 Permittability and Public Acceptability

For all waste scenarios and treatment technologies, effluent discharge permits would likely be required. It is likely that the liquid effluent will require additional processing for solids removal and neutralization, such as in a wastewater treatment plant, prior to discharge. Ultimately, discharge to surface waters would be regulated under the Clean Water Act and would require National Pollutant Discharge Elimination System (NPDES) permits (or state equivalents). For SCWO treatment, air permits under the Clean Air Act and comparable state programs may also be required. For treatment of RCRA-regulated waste streams (such as listed or characteristic industrial wastes), a RCRA Part B permit would most likely be required. In terms of the waste scenarios defined in Section 2, this situation would likely

apply to the electroplating wastes, painting waste, and OB/OD treated wastes. If a SCWO unit were to meet the RCRA definition of a "Totally Enclosed Treatment Unit," then no Part B permit would be needed. This definition, however, requires that the treatment unit be located immediately adjacent and be physically connected to the source of waste generation. Since this configuration seems unlikely for the defined waste scenarios, the requirement of a permit is assumed for all cases.

Under CERCLA programs, formal permits for treatment options are not normally required for on-site treatment. However, treatment and performance standards that would apply under the respective permit programs would not be eliminated (only the formal requirement for the permit).

In addition to the above-noted permit requirements, potential Land Disposal Restrictions (LDRs) promulgated under RCRA may require consideration. The ability of SCFs to meet LDRs for specific RCRA wastes may require verification through testing.

Both the SFE and SCWO systems may have a higher level of public acceptability than more conventional alternative technologies [23]. For example, because SFE processing does not leave a solvent residue in the matrix after treatment, it is considered to be a publicly acceptable alternative to conventional extraction. Similarly, SCWO may be considered to be favorable compared to incineration as the air emissions from SCWO processing are projected to be innocuous. In particular, SCWO does not generate NO_x air emissions. Also, if necessary, effluent streams from SCWO can be contained and monitored prior to discharge. In fact, environmental organizations have reportedly endorsed the use of SCWO technology [23].

4.2.8 Operational Reliability and Demonstrated Performance and Safety Data

Operational reliability and demonstrated performance and safety data are important criteria in the evaluation of SCF technologies. However, to date very little data concerning system downtime or long-term performance are available since most SFE and SCWO units are

available only at the pilot-scale. CF Systems claims to have demonstrated a 90% system availability of a commercial SFE unit [10]. No long-term reliability data were found for SCWO units. System performance evaluation can be based only on attained destruction or removal efficiencies. Specific efficiencies pertinent to the specified waste scenarios were discussed in Subsection 4.2.1.

4.2.9 Cost-Effectiveness in Comparison to Alternative Methods
4.2.9.1 Approach and Basis

To evaluate the potential use of supercritical fluid technologies at Army installations, a preliminary economic analysis has been conducted. The results of this analysis will allow a comparison of costs associated with current treatment and disposal methods with the potential costs estimated for supercritical fluid technology treatment of the same waste scenario.

It must be noted that the available cost information for supercritical fluid technologies is limited. As discussed in Section 3, a limited number of pilot-scale units are available for either SCWO or SFE treatment. Only one full-scale SFE unit has been constructed, and no full-scale SCWO units have been built although large-scale pilot units are operating. Additionally, the waste scenarios described in Section 2 have not been widely tested using SFE or SCWO, adding to the uncertainty in the economic analysis. Finally, since some of the waste scenarios involve soil and explosives processing, uncertainty is involved in the materials-handling issues associated with pumping and treating slurried soils and explosives. Because of the uncertainty involved in the waste processing and the limited amount of cost information available, cost ranges are presented in this section.

Of the waste scenarios described in Section 2, not all appear to be amenable to treatment by SCF processes. The waste scenarios determined to be most amenable from the technical standpoint are the centralized treatment scenario of 456 tons/year of OB/OD treated waste consolidated from four facilities, the 3,900 yd^3 of explosives-contaminated lagoon sediments to be remediated in a 3-year period, and the total of 38,500 gal/year of waste paint, solvents,

and strippers. Although treating other contaminated soil, such as chlorinated hydrocarbon contamination, by SCF treatment options would also be technically feasible, the cost per ton of soil processed may be similar to the costs estimated for the explosives-contaminated lagoon sediments for comparable soil quantities (depending upon treatment kinetics and other waste-specific characteristics). Therefore, the lagoon sediment scenario will be evaluated as an example of treatment of various contaminated soils and sediments.

For analysis purposes, the three scenarios are all assumed to be treatable by SCWO. As discussed in Section 3, SCWO appears to be a technically feasible alternative for destruction of these wastes and treatment of contaminated materials. Because the solvents and strippers found in the combined paint waste may have some recycle value and because solvent and stripper recycle would eliminate the need to destroy that portion of the waste, SFE treatment will also be evaluated for the paint waste scenario. Although SFE treatment of explosives-contaminated soil or hydrocarbon-contaminated soil may also be technically feasible, these scenarios will not be economically evaluated. The safety precautions necessary to make extraction of explosives a feasible alternative are currently uncertain. Quantities of hydrocarbon-contaminated soil vary greatly and could not be specified. Thus, the economic evaluation would be based upon speculation.

O&M cost ranges for the SCWO and SFE units have been supplied by industry vendors. Costs provided by vendors consisted of projections for total capital cost, and no breakdown of cost components was provided. Although the costs include all equipment and piping required for the unit as identified by the vendors, other pre- and post-treatment materials-handling equipment will be required for each of the scenarios. The additional equipment requirements will be discussed individually. Because the scenarios were developed for generic sites, costs to transport the wastes to the beginning of the treatment unit and transport and dispose of any wastes generated are not included. Transportation costs to the centralized facility to treat OB/OD treated wastes are not included. Wastes to be disposed of will be noted with the discussions of individual equipment requirements as appropriate.

The following general assumptions have been made in evaluating the cost-effectiveness of treating the selected waste scenarios by SCF technologies:

- No excavation, disposal, or transportation charges to the unit (including the centralized unit) have been included in the cost analyses. In each case, costs are for only those units specified. These include materials preparation and SCF unit processing steps.

- All utilities and roads are assumed to be provided by the Army Installation to the point of use by the SCF system.

- The potential cost for permitting or regulatory approval of the SCF unit is not included.

- An 8% annual interest rate and a 5-year service life (based on conservative vendor projections of reactor life) have been assumed for purposes of present-worth calculations.

OB/OD Waste — To effectively treat the RDX/HMX, the solid explosives would need to be hydrolyzed in a caustic solution. Work conducted by Los Alamos Laboratory indicates that triple-based propellant can be effectively hydrolyzed using sodium hydroxide [13]. This hydrolysis yields a water-soluble, non-explosive product. Since reactor clogging was experienced at Los Alamos, a dilution of 1:10 with water was required [13]. A lesser dilution may be possible, but the minimum dilution for a given diameter reactor would have to be determined on an individual basis. The SCWO reactor for the first OB/OD treated waste (RDX/HMX mixture) would be required to operate 260 days/year, based upon the projected throughput of approximately 9,600 gpd to treat wastes from four facilities. The second OB/OD treated waste scenario (centralized treatment of stockpiled explosive materials) would require an approximate throughput of 116,800 gpd, 260 days/year. Assuming that materials-handling steps similar to those used in the Los Alamos project would be required for the explosives mixture, the following equipment in addition to the SCWO unit and associated equipment would be needed to process the OB/OD treated waste:

- Heated, stirred tank for hydrolysis.
- Heated caustic tank and pump.
- Site work and installation.

- Stirred dilution tank.

Explosives-Contaminated Lagoon Sediments — For SCWO treatment of the explosives-contaminated lagoon sediments, the material would have to be slurried to about 20% solids prior to pumping. Additionally, a supplemental organic source would need to be added to increase the organic content of the stream to the targeted 10%-25% for autogenous operation. The 5,000 gpd SCWO unit would be required to operate 260 days/year in order to process 3,900 yd³ of sediment in 3 years. The 3-year time frame was taken to be a typical schedule for an Installation Restoration Program. The following equipment would be needed in addition to the SCWO unit itself:

- Site work and installation.
- Chemical feed tank and pump.
- Mixing tank for slurrying.
- System for separation of soils from water after treatment.

After processing, the treated soils could be considered clean for redisposal.

Mixed Paint Waste Treatment by SCWO — SCWO treatment of the mixed paint wastes would also involve a dilution step. In this case, the dilution is needed to reduce the waste stream organic content to within the acceptable range of 10-25% in order to maintain autogenous conditions. For this ongoing industrial waste scenario, the annual volume of waste to be treated is such that a 1,500 gpd skid-mounted reactor could process the required amount of waste by operating approximately 4 weeks/quarter. It may be possible to lower the cost of the system by optimizing the reactor size and increasing the operating frequency. In addition to the SCWO unit, the following equipment would be required:

- Stirred dilution tank.

- Site work and installation.

- Separation process for removal of salts formed during oxidation. Although removal in the supercritical phase is possible, additional separation may be required depending on effluent limitations.

Mixed Paint Waste Treatment by SFE — SFE treatment of the mixed paint waste would result in a concentrated extract stream containing the targeted solvent or stripper. The waste would be diluted to a pumpable form and fed to the SFE reactor countercurrently to the supercritical fluid. The extract stream would be withdrawn, the extract separated from the solvent, and the fluid recompressed and recycled to the reactor. The unextracted waste components would be withdrawn from the bottom of the reactor. This unit would be expected to operate approximately 40 days/year (2 weeks/quarter) based upon a presumed throughput of 5,000 gpd. This use of a smaller unit operated more frequently may reduce the unit capital costs and, therefore, overall costs. However, cost data for other reactor sizes are not available and the unconventional nature of the system precludes the use of traditional scaling factors to adjust the available cost projections. Additional equipment required for SFE processing of mixed paint wastes is as follows:

- Mixed dilution tank.
- Site work and installation.

The unextracted media would have to be subsequently treated and disposed. Depending on the solvent and process conditions chosen, the material may have organic and inorganic constituents. Depending on the regulatory status of the original waste constituents, this material may require RCRA disposal.

4.2.9.2 Range of Potential Costs

The projected cost ranges associated with treatment of the described waste scenarios are presented in Tables 4-1 and 4-2. As mentioned previously, estimated cost ranges for SCF technology processes were supplied by various vendors. Since cost ranges were provided for specific unit sizes, the high and low ends of each range were used for the purpose of this report. This high end conservative assumption is based on the uncertainty of using treatment methods for the selected wastes and media that have not yet been fully proven. The low end cost was included as a more optimistic, yet still realistic, possibility. Additionally, a 10% contingency has been added to each of the scenarios in both the high- and low-end estimates. A 10% contingency was selected because it is assumed that the

Table 4-1

Estimated "High-End" Capital and O&M Costs for SCF Treatment of Selected Waste Scenarios

Waste Scenario (Quantity)	SCF Technology	SCF Unit Cost ($)	Additional Capital Costs ($)	10% Contingency ($)	Total Capital ($)	Annual[d] O&M ($)	Total P/W 5-Year Cost ($)	Unit Cost ($)
RDX/HMX OB/OD Waste (456 tons/year)	SCWO	6,000,000	470,000	650,000	7,120,000	1,000,000	11,110,000	4,900/ton[b]
Centralized OB/OD Waste (15,000 tons)	SCWO	10,000,000	1,030,000	1,100,000	12,130,000	940,000	14,540,000	1,000/ton[e]
Explosives-Contaminated Soil Treatment (3,900 yd³)	SCWO	6,000,000	470,000	650,000	7,120,000	1,000,000	9,700,000	2,500/yd³ [a]
Mixed Paint Waste/Solvents/Strippers (38,500 gal/year)	SCWO	2,000,000	290,000	229,000	2,519,000	78,000	2,830,000	15/gallon
Mixed Paint Waste/[c] Solvents/Strippers (38,500 gal/year)	SFE	2,500,000	290,000	280,000	3,070,000	35,000	3,210,000	17/gallon

[a]A 3-year project duration was assumed due to the small quantity of material involved in the IR Program.
[b]Assumes a TSD facility processing a total of 456 tons/year of off-specification explosive material.
[c]A range of costs were not available for SFE processing.
[d]Based on vendor information.
[e]A 3-year project duration was assumed.

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Table 4-2

Estimated "Low-End" Capital and O&M Costs for SCF Treatment of Selected Waste Scenarios

Waste Scenario/Quantity	SCF Technology	SCF Unit Cost ($)	Additional Capital Costs ($)	10% Contingency ($)	Total Capital ($)	Annual[d] O&M ($)	Total P/W 5-Year Cost ($)	Unit Cost ($)
RDX/HMX OB/OD Waste (456 tons/year)	SCWO	2,000,000	470,000	250,000	2,720,000	500,000	4,720,000	2,100/ton
Centralized OB/OD Waste (15,000 tons)	SWCO	6,000,000	1,030,000	700,000	7,730,000	940,000	10,140,00	700/ton[e]
Explosives-Contaminated Soil Treatment (3,900 yd[3])	SCWO	2,000,000	470,000	250,000	2,720,000	500,000	4,010,000	1,000/yd[3] [a]
Mixed Paint Waste/ Solvents/Strippers (38,500 gal/year)	SCWO	1,250,000	290,000	154,000	1,700,000	50,000[c]	1,900,000	10/gallon
Mixed Paint Waste/[b] Solvents/Strippers (38,500 gal/year)	SFE	2,500,000	290,000	280,000	3,070,000	35,000	3,210,000	17/gallon

[a] A 3-year project duration was assumed due to the small quantity of material involved in the IR Program.
[b] A range of costs was not available for SFE processing.
[c] $650/8-hour day - 1 shift, 20 days/quarter.
[d] Based on vendor information.
[e] A 3-year project duration was assumed.

vendor-supplied costs contained contingency factors. Although either capital or O&M cost data were available from a number of vendors, data were chosen for use in this report for which both capital and operating and maintenance (O&M) costs were available. Also, costs were chosen that were for units of comparable size to those estimated for each waste scenario. Using an 8% annual interest rate and 5-year project life, a total 5-year project cost has been calculated. This total cost has been divided by the total quantity of material to be processed, thus yielding a unit cost for each waste scenario evaluated. These costs are also presented in Tables 4-1 and 4-2.

The limitations inherent in the data used to develop these cost estimates should be recognized in interpreting these results. As previously noted, capital costs are based upon general equipment cost data provided by vendors and are based in large part upon projections from pilot-scale units. These costs have not been specifically developed for the particular waste scenarios due to limitations in available data. Waste stream specific performance data, as well as required materials of construction, materials handling and residuals information, would be required to prepare specific cost estimates.

Similarly, general O&M cost data have been provided by equipment suppliers. These data reflect neither waste-specific material, labor, and energy requirements nor site-specific material, labor, and energy costs. For both capital and O&M costs, limited data were available from vendors. As such, costs presented are for system sizes available and not necessarily for the optimal system size to process the given waste.

As a result of these limitations, the projected unit treatment costs for SCF technologies are approximate in nature, for the purpose of conceptual comparison only to other management alternatives.

The unit costs for treatment of the various waste scenarios appear to be somewhat higher than costs for alternative treatment technologies. For example, the estimated cost for SCWO treatment of explosives-contaminated lagoon sediments is in the range of $1,000/yd^3 to $2,500/yd^3 as compared to an estimated cost in the range of $500 to $1,500/ton, for the

quantities of material to be treated in these scenarios, for incineration as shown in Figure 4-1. For very large quantities of materials, incineration costs may be as low as $200/ton. Assuming a typical soil density of 2,300 lb/yd^3, this corresponds to $575 to $1,725/yd^3 for incineration. The cost for SFE treatment of mixed paint waste has been estimated at $17/gallon and SCWO treatment of the same waste in the range of $10 to $15/gallon as compared to $2.50/gallon for a conventional tolling arrangement for waste destruction [63].

No OB/OD treatment costs are currently available to serve as a comparison. A range of $2,100 to $4,900/ton was calculated for SCWO treatment of 456 tons/year of an RDX/HMX mixture. The unit costs, however, are significantly lower for destruction of larger quantities of OB/OD treated wastes. The scenario of 15,000 tons of explosive waste to be treated in a 3-year period has a cost of $700 to $1,000/ton. This cost does not include washout procedures or transportation.

When comparing SCF technology waste treatment to more conventional treatment methods on an economic basis, the following items must be considered:

- SCF is an innovative technology and thus some of the cost is associated with the uncertainty of using a nonstandard treatment method. By contrast, costs for technologies such as incineration are relatively well-defined because of extensive operational experience. Additionally, the possibility exists that SCF equipment and operating costs will decrease as the technology develops further.

- The available cost data for operating units are limited. Cost data are available from vendors for only a few existing pilot-scale units. Since cost information was available for only certain reactor sizes, the reactor size and configuration was not optimized. Instead, available cost data most nearly matching the desired reactor capacity was used.

- The costs projected in this study are generally similar to those projected in the Naval Civil Engineering Laboratory (NCEL) study [62]. Based upon the treatment scenario developed in that study, for a SCWO unit to process 830 tons/year of liquid organic waste for a 5-year projected reactor life with an 8% annual interest rate, the present-worth unit cost would be approximately $2,500/ton.

Site Size-Tons
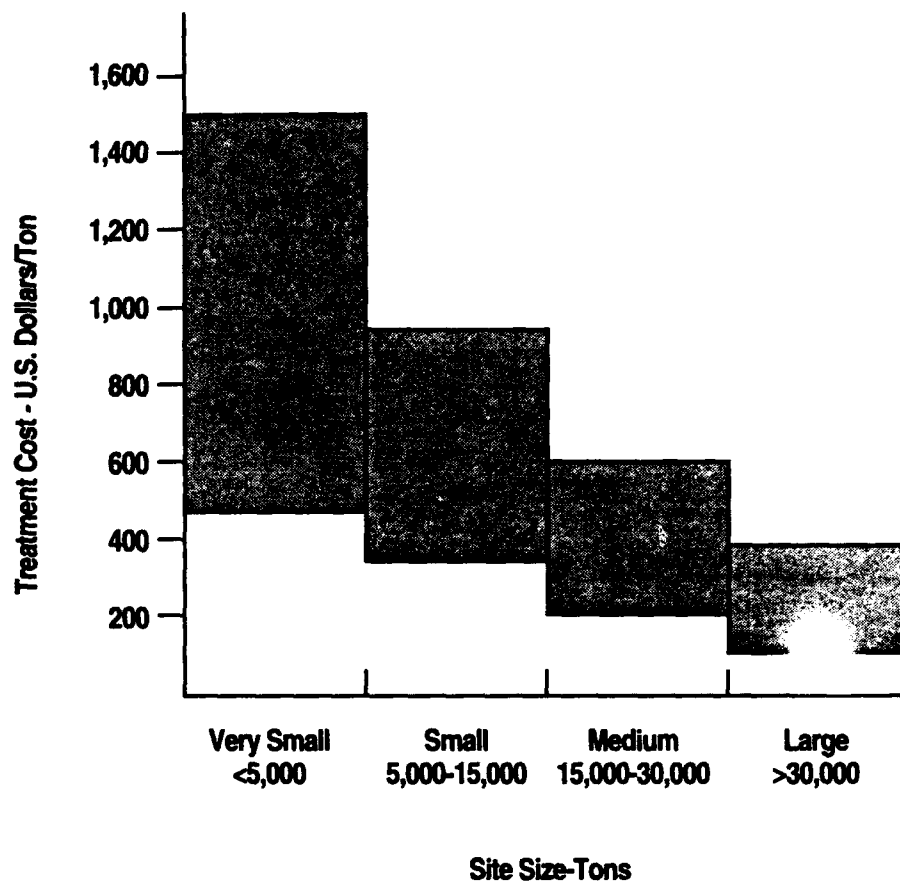
Source: The Hazardous Waste Consultant

FIGURE 4-1   EFFECT OF SITE SIZE ON INCINERATION COSTS

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4.2.9.3 Cost Sensitivity Issues

In this section, a general discussion of potential areas of cost savings in SCF technologies is presented. In some cases, these savings may result from the opportunity to delete or minimize the need for certain process units (for example, solids separation equipment which would not be required for certain liquid wastes). In other cases, cost savings may result from future process improvements that may result from additional research and technology development. These or similar factors may help support the more optimistic (lower) costs presented in the previous section. The following discussion may help guide future USAEC activities relative to the development of SCF technologies.

In order to evaluate potential areas for cost savings in SCWO processing, several vendors (General Atomics, Thar Designs, Modar, and Kem-Shredder) were contacted as follow-ups to the initial conversations reported in Subsection 3.4. The vendor comments, along with information from the NCEL cost estimate [62] were used to evaluate areas of possible cost savings in SCWO processing.

In the cost estimate prepared by A.D. Little, Inc. for NCEL [62], costs for individual components of an SCWO system, based on a design by the NCEL were estimated. This design is not necessarily representative of the basic designs used by the SCWO vendors and therefore may not directly correspond to the cost ranges discussed in this report. However, this detailed cost estimate provides a breakdown of contributing cost factors that might be useful for purposes of evaluating potential cost savings associated with future developments in SCWO. Vendor information will be used as applicable to supplement the information from the cost estimate.

It must be noted that it is difficult to make generalities regarding SCWO system costs because they are very strongly tied to specific wastes to be treated. As an example, wastes that form "sticky salts" during treatment will require more costly solids separation schemes than will be required for wastes not forming "sticky salts." Wastes likely to form these salts include halogenated solvents requiring neutralization because of the acidic conditions

generated during processing. Other wastes, such as many explosive wastes, would not generate these salts and would require less complex solids separation equipment.

Areas of potential savings with further development include:

- Improving system materials of construction, specifically with respect to corrosion resistance, will increase system life, thus lowering overall project cost per unit of waste processed. Improving the materials of construction could potentially increase the useful life of not only the reactor itself, but also that of other auxiliary equipment such as heat exchangers and feed systems.

- Although the NCEL cost estimate [62] does not specify a particular organic waste for processing, the system design appears to be a conservative approach. For example, solids separation equipment is included both upstream and downstream of the SCWO reactor itself. Such conservatism is also built into the vendor cost estimates. Without knowledge of the specific wastes to be treated, costs must be estimated based on conservative assumptions about the wastestream. Much of the equipment and its associated cost, could be eliminated if the SCWO system design is optimized for a targeted wastestream.

  Table 4-3 is a partial summary of the costs tabulated in the NCEL cost estimate [62].

- For the conditions and configuration shown in that report, the waste mixing and pressurization system account for 13% of the Total Installed Equipment cost, or 9% of the Total Capital Investment cos. For homogenous, liquid systems, mixing may be minimal. Also, in some cases, it may be possible to pressurize only the waste feed or oxidant stream, and not both.

- The solids separation system is 16% of the Total Installed Equipment, or 11% of the Total Capital Investment. As discussed elsewhere, this separation system may be unnecessary for certain wastes which generate minimal solids during processing. Likewise, for specific waste applications, the pH adjustment system (representing 3% of the Total Installed Equipment Cost or 2% of the Total Capital Investment) may not be needed. The Offgas Treatment and Monitoring System accounts for 11% of the Total Installed Equipment or 7% of the Total Capital Investment. Based on off-gas data from treatability tests, off-gas treatment may not be required. The Liquid Oxygen Feed System represents 16% of the Total Installed Equipment or 11% of the Total Capital Investment. Alternative oxygen supplies could potentially save a portion of this expense.

Table 4-3

Approximate Cost Contributions from
Various SCWO Subsystems as Presented by NCEL [62]

System Description	Capital Investment (1992 $)	% Total Installed Equipment	% Total Capital Investment
Hazardous Waste Mixing and Pressurization System	540,000	13	9
Start-Up Heater and Recirculation System	614,000	15	10
Solids Separation System	652,000	16	11
Sampling and pH Adjustment System	108,000	3	2
Liquid/Vapor Separation System	478,000	12	8
Off-gas Treatment and Monitoring System	432,000	11	7
SCWO Reactor System	387,000	10	6
Liquid Oxygen Feed System	646,000	16	11

These potential areas of savings are based solely on the NCEL cost estimate [62], and the percentage of capital saved may not be directly applicable to other cost estimates. However, this breakdown is useful in illustrating the potential benefits of a thorough evaluation of specific waste and its characteristics when considering SCWO processing.

- Conversations with various experts in the field of SCWO technology indicate that optimization of kinetics and reactor design will lower the overall project cost. Reactor design includes both optimization of the reactor size and operating conditions through kinetic evaluation of the specific waste(s) to be treated as well as design of a solids separation and handling scheme to accommodate the specific solids generated during the targeted wastedestruction. Tailoring the system for the specific targeted waste will lead to cost savings because the reactor itself will be optimized and solids separation equipment will be designed as needed. In cases such as in the destruction of many energetic materials, where few precipitates are formed and no "sticky salts" are generated, a complex reactor design and solids separation step would not be needed. A more costly reactor may be required for wastes, such as chlorinated hydrocarbons, which would require neutralization and consequently generate "sticky salts" during processing.

  The NCEL report [62] indicates that the reactor costs represent only about 10% of the total installed equipment cost, implying that the impact of reactor cost reduction may not be the driving force in system cost reduction. The solids separation unit in the NCEL report accounts for 16% of the total installed equipment cost.

- Since SCWO vendors commonly purchase components (such as pumps, tanks, valves, etc.) from suppliers, these pieces of equipment are not necessarily optimized for use in SCWO processing. If SCWO vendors manufactured some of these pieces, system life could probably be extended by optimizing the component design, and additional cost savings could be realized by not marking up the cost of the component equipment through the use of an additional vendor. However, the unit cost for these specialized, low quantity parts may be higher than for more common, off-the-shelf components.

- Batch processing has the potential for cost savings in selected cases. For example, in the case of off-specification munitions, batch SCWO processing could potentially be used to simultaneously remove and destroy the energetic material, thus eliminating the need for an extraction procedure prior to SCWO treatment. The potential savings associated with the elimination of this step would need to be balanced against increased energy costs associated with repeatedly pressurizing and heating the reactor. Batch processing could also potentially eliminate problems associated with salt buildup in the reactor because the batch reactor would be more accessible than continuous flow reactors in which reaction occurs in a pipe. For "sticky salts," this feature of a batch reactor could eliminate some of the O&M costs.

While these potential cost savings cannot be quantified at the present time, this discussion indicates that SCF technologies may become more cost effective in the near future.

4.2.10 Consideration of System Materials of Construction

Because of the severe reaction conditions and often corrosive materials present in SCWO processing, system materials of construction are a consideration in SCWO technology evaluation. Corrosion of the reactor materials is a primary contribution to the relatively short service life currently projected for SCWO systems. Increasing the corrosion-resistance of the reactor materials therefore would increase the reactor service life, and decrease the unit cost of material processed. Corrosion resistance and resistance to plugging are also factors in designing valves throughout the SCWO system.

Research is currently being conducted in an attempt to extend reactor and valve lives and potentially lower SCWO unit capital costs. Research in the area of reactor materials of construction is focusing primarily on the development of corrosion-resistant coatings used to line the reactor. The reactor material itself must then only possess the required structural properties to withstand the temperatures and pressures within the system. Both ceramic and metallic coatings are being investigated.

SECTION 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

5.1.1 General

In the past several years, SCF technologies have been the subject of extensive research for a variety of applications. These applications include the areas of food and pharmaceutical processing, oil refining, and waste separation and destruction.

SCF technologies currently in use include Supercritical Fluid Extraction (SFE) and Supercritical Water Oxidation (SCWO). SFE processing uses the unique solvating power of supercritical fluids to extract one or more organic components from a mixture forming a concentrated extract stream. The extracted component is often a valuable product or a hazardous constituent. SCWO processing uses an oxidative, supercritical environment to destroy organic compounds, resulting in innocuous end products. Both SFE and SCWO processes have been demonstrated at the pilot-scale. Additionally, a full-scale SFE unit has been developed.

Generally, organic materials are amenable to processing by SFE or SCWO techniques, given the proper set of operating conditions. Additionally, SCWO processing may be used to separate inorganic materials that form insoluble salts under supercritical conditions.

Materials-handling issues will present one of the greatest challenges to field implementation of SCF technologies. Since SCWO processing has traditionally been a continuous operation, it is more amenable to liquid wastes. Any solid material to be processed must be slurried to a pumpable form. This requirement means that any solid carrier materials would need to be reduced in size prior to slurrying. Additionally, constraints on particle sizes and morphology may exist in order to control plugging in valves or in the reactor itself. It may be possible to operate SCWO systems in a batch-mode, but this operation has not been demonstrated except in bench-scale systems. Also, the economic benefits of not slurrying

or dissolving solid materials prior to treatment must be balanced against the energy cost of repeatedly heating and pressurizing the batch reactor. Sequential batch reactors may eliminate some of this burden. Since SFE processing can be conducted on a batch basis, the same slurrying requirements would not be necessary. In the case of SFE treatment, soil or other carrier materials could be loaded in the reactor and the constituent extracted batch-wise. SFE processing results in a concentrated extract stream that must then undergo subsequent handling in the form of product recycling, disposal, or destruction.

Another materials-handling consideration is reactor corrosion. The oxidative environment maintained during SCWO processing can lead to severe corrosion of the reactor walls as well as the related valving. Development of corrosion-resistant reactor materials or coatings is a major current area of research in SCWO processing. SFE processing is typically conducted under less severe conditions and thus corrosion is not as critical an issue as in SCWO processing.

Processing of explosives and explosives-contaminated materials will require specific materials-handling considerations. In the case of SCWO processing, safety considerations must be addressed for the steps (such as size reduction and slurrying) prior to feeding the explosive material into the reactor. If explosive materials are to be treated by SFE, the extract stream will have a high explosives concentration and may be prone to detonations. There is a potential for adding diluent to the extract stream to reduce the safety hazards.

5.1.2 Summary

To evaluate the applicability of SCF technologies to Army installations, the following waste scenarios were developed:

- Waste paint/solvent.
- Explosive materials previously destroyed by OB/OD.
- Electroplating waste.
- Explosives-contaminated lagoon sediment.
- Packing plant wastewater.
- Soil contaminated with chlorinated hydrocarbons, metal, and explosives.

These scenarios were evaluated based on the following criteria:

- Capability of removing and destroying hazardous waste components to concentrations defined in applicable laws and standards.

- Ability to remove or destroy surface contamination without complete destruction of the carrier material.

- Nonspecificity in treating varieties of hazardous waste materials.

- Identification of waste residues generated.

- Potential safety hazards associated with treating explosives-contaminated materials.

- Capability of treatment at the source or site of the contamination within the schedule of an Installation Restoration (IR) Program.

- Permittability and public acceptability.

- Operational reliability and demonstrated perfc.~mance and safety data.

- Cost-effectiveness in comparison to alternative treatment methods.

- Consideration of system materials of construction.

Based on these criteria, it was determined that one scenario, electroplating waste, was not amenable to SCF processing due to its essentially inorganic nature. The waste paint and solvent waste could probably be treated by either SFE or SCWO processing although waste-specific treatability data are limited. SCWO processing would destroy the organic content of the waste and potentially the inorganic materials would be separated by precipitation in the supercritical phase. SFE treatment would yield an organic-rich extract stream with other constituents remaining unaffected in the extraction vessel. The potential exists to use this technique to recover specific solvents from the mixture, depending on individual constituent solubilities. A variety of chlorinated hydrocarbons have been demonstrated to be treatable by SCWO and SFE techniques.

SCWO processing of explosives has been demonstrated for TNT, DNT, and NG. To alleviate safety concerns as well as potential reactor plugging issues, explosives materials have been hydrolyzed and diluted with water prior to treatment by SCWO. Explosives-

contaminated soils would be slurried in water prior to being fed to the reactor. Repacking plant wastewater could be fed as produced into the SCWO reactor. Explosive materials in the form of contaminated sediments and OB/OD wastes contained in repacking plant wastewaters may present a safety hazard for SFE processing. Although extractions without detonations have been demonstrated by adding a diluent to the extract stream, in other areas extract stream detonations did occur. Conducting SFE operations without encountering these problems would require further study.

A variety of contaminated soils could potentially be amenable to SCF treatment processing. Potential contaminants include chlorinated hydrocarbons, petroleum products, and explosive materials. For each individual soil scenario, the proper SCF technology and operating parameters would be chosen based on site-specific considerations such as contaminant type and concentrations and cleanup goals. Waste and site-specific treatability testing would generally be needed to establish treatment conditions.

Unit costs (including capital and O&M) for treatment of the specified waste scenarios by SCF technologies were projected to be in the following ranges:

- RDX/HMX OB/OD Waste SCWO, 456 tons/year, waste from 4 facilities $2,100   to $4,900/ton

- OB/OD Waste SCWO, 15,000 tons $700   to $1,000/ton

- Explosives-Contaminated Soil Treatment by SCWO, 3,900 yd^3 $1,000   to $2,500/yd^3

- Mixed Paint Waste/Solvents/ Strippers by SCWO, 38,500 gal/year $10   to $15/gallon

In general, these unit costs presented are higher than costs associated with more conventional treatment technologies. The higher cost may be, at least in part, attributable to the following factors:

- SCF is an innovative technology with no full-scale experience for the waste that is being considered in this evaluation.

- Available cost data are limited and may not be completely applicable to the selected waste scenarios.

- Due to limitations in available cost information, the reactor configurations and costs were not optimized to the specific waste scenarios.

5.2 RECOMMENDATIONS

Due to the projection of higher costs associated with SCF technologies as compared to more conventional treatment methods, SCF technologies are not recommended for implementation by USAEC at this time. SCWO treatment of the following waste scenarios is promising based on technical evaluation:

- OB/OD treated waste.
- Exposure-contaminated lagoon sediment.
- Soils contaminated with solvents and petroleum products.

Some promise of future applicability lies in potential cost savings that may result from additional development. In addition, regulatory factors, which may render other options, such as incineration or OB/OD less favorable, may make the development of SCF systems for the treatment of such wastes more desirable in the future.

Given the current level of basic and applied research in the SCF field, it should not be necessary for USAEC to directly pursue fundamental research in areas such as materials handling and materials of construction. However, application of potential advances in such areas to wastes of interest to USAEC may ultimately require bench and/or pilot-scale testing.

Should technical advancements make SCF technologies more cost competitive, the following steps are recommended prior to undertaking a demonstration effort by USAEC:

- Refinement of the waste scenario in terms of waste quantity and quality is recommended.

- Conduct a chemical analysis of the wastes to be treated to determine constituents, physical and chemical properties of the mixture, potential corrosivity, and potential degradation products under typical SCWO conditions. Evaluate the chemical characteristics of the waste with respect to known wastes being treated by SCWO.

- Determine the kinetic parameters to be used during SCWO treatment through bench-scale testing. Degradation products (solids, liquids, and gases) as well as corrosion-resistance of targeted materials of construction could be determined during this testing. Additionally, if pilot-scale testing appears favorable, operating parameters could be optimized at pilot scale. The results of this testing should be evaluated with respect to kinetic results from known SCWO processes.

- Based on the information from the bench-scale testing, a conceptual design for the reactor and associated equipment should be performed. Kinetic data would determine the reactor size, while solid products formed and their properties would determine the reactor configuration. The additional equipment required for operation, such as heat exchangers, mixers, and solid separation units, would be selected based on the characteristics of the waste feed stream and SCWO degradation products.

- An economic analysis of a particular system based on reactor configuration and required supplemental equipment should be conducted. It seems likely that cost savings could be realized if the SCWO system is tailored to a specific application as opposed to design of a generic SCWO unit.

If the detailed economic analysis which results from waste-specific characterization indicates that the process is economically viable, pilot-scale testing should be conducted to provide proof of concept data, as well as scale-up and design information.

SECTION 6
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